Recovery of Zinc from Ash of Galvanizing Plant by Hydrometallurgical Route

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Declaration

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or Diploma.

Shah Najiba

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Abstract

Zinc ash is a discarded material of galvanizing plant and consists mostly of oxidized zinc that forms on the surface of molten zinc metal in galvanizing pot. The ash is removed from the top of galvanizing baths by skimming or straining and discarded. Both hydrometallurgical and pyrometallurgical processes can be used for recovery of zinc from ash. But, hydrometallurgical methods are comparatively clean and can be adapted in small and medium scale industries. In this work, hydrometallurgical path is followed to recover zinc from discarded ash of galvanizing plant.

The composition of the supplied ash was determined by XRF analysis and it was found that the ash consists of around 62% zinc along with other impurities like chlorine, iron, lead, aluminium, copper, etc. Chlorine cannot be tolerated in the subsequent electrowinning of zinc metal, as even a very small amount in the electrolyte is extremely damaging to the electrode and operator of the electrolysis.

Two methods were tried to remove chlorine: calcinations and washing with distilled water. Calcination can remove chlorine, but because of high iron content in this sample, a stable complex of iron with zinc and oxygen was formed which is not soluble in diluted sulfuric acid. Washing with distilled water was tried and it was found to be satisfactory. The parameters of liquid/solid ratio, temperature and time were optimized to minimize energy required for washing. Washing with distilled water at liquid/solid ratio of 10:1 (ml/gm) for 30 minutes at 80^{o}C removed 80% of chlorine present in the sample. It was found that zinc in minor level (around 2%) is also lost in distilled water.

Zinc ash was then leached in dilute sulfuric acid. Leaching parameters of particle size, concentration of leaching reagent, liquid/solid ratio, time and temperature were optimized to obtain maximum amount of zinc in leach liquor. Optimum leaching parameters were found as: mesh size of -200+270 mesh, concentration of H_2SO_4 of 3.2 M (~17% H_2SO_4), liquid/solid ratio of 5, leaching time of 140 minutes and leaching temperature of 70^{o}C. With these optimum

conditions, the concentration of zinc in leach liquor was found as around 117 g/L (which is about 94% of the zinc present in the sample).

The leach liquor was purified with respect to soluble impurities. Iron is released into the solution mostly as Fe^{2+} during leaching. For precipitation of iron, at first it was converted into Fe^{3+} by oxidation with sparging air and addition of oxidising agent MnO_2. After oxidation, Fe^{3+} is precipitated by controlling the P^H between 4.5 to 5.2 using $Ca(OH)_2$ to adjust P^H. The leach liquor is filtered to remove precipitates. After removal of iron and aluminum, other impurities are removed by simple cementation technique.

The cementation technique was carried out in three different stages. First stage was carried out by the addition of zinc dust at ambient temperature. This stage removes copper and cadmium as cement. The second stage was carried out at high temperatures of 85^oC in the presence of potassium antimony tartarate, which removes practically all of the impurities. In the third and final step, activated charcoal was added to the purified solution to adsorb other impurities and unwanted organics (if present). The third step is the polishing step. After each step the leach liquor is filtered to remove precipitated impurities.

The electrowinning technique was applied for producing a pure zinc metal from the purified solution. Electrolysis was performed at 30^oC with current densities of 30, 45 and 60 mA/cm^2. The effects of zinc and free sulphuric acid concentrations and current density on the current efficiency were studied. The minimum zinc concentration at which electrowinning should be stopped was found to be in the range of 40 g/l with a sulphuric acid content of >150 g/l.

CHAPTER 1

INTRODUCTION

Zinc is the most used non-ferrous metal next to aluminium and copper. Apart from its major applications (about 70%) in the galvanizing of steel, the other important areas of utilization are as sheets, anodes, castings, chemicals, micronutrients, paints, dry cells, etc. As the usage of zinc increases, the gap between demand and supply is widening. The possibilities of recycling of zinc exist from many of these applications. Out of about 10 million tons per year of zinc production globally, about 30% of zinc is produced from secondary resources.

Almost all metallurgical processes are associated with the generation of wastes and residues that may be hazardous or non-hazardous in nature depending upon the criteria specified by institutions such as the US Environment Protection Agency, etc., that are present beyond permissible limits deemed to be treated or disposed of, and non-hazardous wastes can be utilized for metal recovery or safe disposal. Zinc is in growing demand all over the world. In Bangladesh, a major amount of zinc is imported and therefore processing of zinc secondaries will assist in satisfying the gap between demand and supply to some extent. This report mainly focuses on the current practices and recent trends on the secondary processing of zinc. Attempts were made to develop ecofriendly processes for the recovery of zinc from secondary raw materials.

Recycling of zinc offers both environmental and economic benefits by: (i) reducing the energy required for mining and processing; (ii) reducing volume of material that end up on land filling; (iii) relieving environmental impacts on the land and water; and (iv) conservation of ores [1].
Zinc is the principal raw material in hot dip galvanizing. Zinc ash is a discarded material of galvanizing plant and consists mostly of oxidized zinc that forms on the surface of molten zinc metal in galvanizing pot. The ash is removed from the top of galvanizing baths by skimming or straining and discarded. This study deals with the recovery of zinc as pure zinc metal from

secondary resources, namely zinc ash, produced during the galvanization processes of steel sheets. These wastes are usually composed of variable composition of metallic zinc and zinc oxide and may contain from 50 to 80% total zinc along with some impurities entrained from galvanization process [2]. Among these impurities, small amount of chlorine is extremely harmful to the subsequent electrolysis. Sulfuric acid leaching processes have been investigated to recover zinc selectively from waste materials such as ash of galvanization process. Zinc electrowinning is very sensitive to the presence of impurities in the electrolyte. Electropositive ions co-deposit on cathode zinc and make the product impure. The purification process of zinc electrolyte has been studied. Zinc was recovered from leach solutions by an electrowinning process in which zinc is electrodeposited on aluminum cathodes while oxygen is evolved at lead anodes.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

Hydrometallurgy represents a potentially attractive alternative to pyrometallurgy for the extraction of metals. This route requires less energy and sometimes with careful process design it is possible to use ambient processing temperature. Another important feature of hydrometallurgical processes is that the chemical reactions which are carried out are often far more selective than those encountered in pyrometallurgical treatments. For example, when dissolving a particular mineral from an ore a reagent can usually be found that attacks the wanted minerals but almost leaves untouched the unwanted gangue materials. Thus, the cost of the reagents is related more to the total metal content of the ore rather than the concentration of the mineral in the ore.

2.2 Theoretical Background

2.2.1 Hydrometallurgical Recovery of Zinc

Hydrometallurgy refers to the production of metals or pure compounds with the help of reactions in aqueous solutions. In recent years this definition has been expanded to include the use of organic reagents. It is a process of beneficiation as well as extraction. Hydrometallurgical treatment is usually carried out on low grade ores which are not amenable to pyrometallurgical operations.

Hydrometallurgical processing involves the following steps [3]:

Leaching: During leaching the desired elements (either the value or the gangue) in the ore are selectively dissolved in an appropriate solvent known as the leaching reagent or leachant. Proper leaching may call for some preliminary ore preparation operations such as grinding, sizing, physical beneficiation, roasting etc.

Separation of leach liquor: In this step, the solution i.e. the leach liquor is separated from solid residues by one or more of the various methods of materials separation, viz. settling, thickening, filtration, washing etc.

Recovery of metallic values from leach liquor: The desired solute or the metal in elemental form is obtained in the recovery step. Methods employed to treat the enriched liquor include evaporation, distillation, precipitation, cementation, electrolysis, ion exchange, solvent extraction etc.

Reagent recovery: The leaching reagent is generally recycled after purification and readjustment of composition.

Any hydrometallurgical process consisting of these steps may have one of the following objectives:

- To produce a metal from either crude metal or metal compound that has been prepared earlier by other methods.
- To produce a pure compound that can subsequently be processed to a metal by pyrometallurgical methods. Here hydrometallurgy is only a beneficiation step.
- To produce a metal directly from an ore or concentrate.

Hydrometallurgical processing is characterized by a number of distinct advantages [3]. These are listed below:

- Hydrometallurgical methods are suited for lean and complex ores. With gradual depletion of rich ore deposits, it is becoming increasingly difficult in many situations to apply the conventional pyrometallurgical methods for metal extraction. If there is too much gangue, then processing ores at high temperatures causes wastage of energy as well as problems of slag disposal. An important feature of hydrometallurgical processes is that the chemical reactions which are carried out are often far more selective than those encountered in pyrometallurgical treatments. For example, the siliceous gangue in ore is unaffected by most leaching agents; whereas in pyrometallurgical smelting processes, the gangue must be slagged. Thus the cost of reagents is related more to the total metal content of the ore, rather than the concentration of the mineral in the ore. This is the reason why gold ore containing 10 ppm (10mg/L) can be extracted economically using cyanide solutions whereas smelting of this ore is out of the question.

- Hydrometallurgy allows greater control over every step in processing of ores resulting in recovery of valuable by-products. Metals may be obtained directly in a pure from the leach liquor using one of several methods. Handling of material is also easier.
- Hydrometallurgical operations are often preferable from the point of view of environmental pollution. Thus while pyrometallurgical processing of sulphide ores produce SO_2, leaching of ores keep sulphur in solution. SO_2, liberated during roasting of sulphides as well as during the other steps in pyrometallurgical processing, is not always suited for use in H_2SO_4 production. Even if it is used in acid production, there is still escape of SO_2, in air unless stringent antipollution measures are affected.
- Because of the rapidly increasing cost of metallurgical coke, which is both the main energy source and the main reductant in many pyrometallurgical processes, an aqueous processing route is sometimes favored.
- A hydrometallurgical process may start on a small scale and expand as required. However, a pyrometallurgical process usually must be designed as a large scale operation for reasons of process economy.

Hydrometallurgical processing is characterized by a number of distinct disadvantages [3]. These are listed below [3]:

- Hydrometallurgical treatments are usually carried out at less than $100^{o}C$ and the process streams are dilute (less than 1 mol/L of solute). The significantly lower operating temperatures used in hydrometallurgical processes, in general, give low reaction rates. Thus large volumes of solutions are to be handled for relatively smaller metal outputs. This requires considerable amount of handling as well as space.
- Water has a high heat capacity. Therefore, to heat dilute solutions above ambient temperatures considerable amounts of energy must be expended. However, this disadvantage is to some extent offset by utilizing by-product of power generation or a pyrometallurgical process.

- Some reagents are expensive and must be recycled or regenerated for economy.
- Reaction rates are lower at room temperatures as compared to processing at high temperatures. Hence tonnage capacity of a plant is lower as compared to that obtainable in pyrometallurgy.

2.2.2 Leaching

Since hydrometallurgical processes are concerned in the main with the treatment of metal ions in solution, the first consideration should be the dissolution or leaching of the metal. For a successful leaching system there are a number of essential aspects of processing which must be fulfilled and there are a number of features which are desirable if costs are to be kept to a minimum.

2.2.2.1 Essential Features

i) the valuable metal must be soluble in an economically usable solvent,
ii) the metal must be economically recoverable from solution, and
iii) any impurity elements which are co-extracted during leaching must be capable of further separation from the solution.

2.2.2.2 Desirable Features

i) The gangue minerals should not consume excessive amounts of solvent,
ii) the solvent should be recoverable (or capable of regeneration) for recycle,
iii) the feed material should be free of clay minerals, as these make separation of leach liquor from the treated solids difficult,
iv) the feed material should be permeable to the solution allowing direct contact between the solvent and the phase to be dissolved, and providing a high liquid/solid area for reaction for a given mass of material, and
v) the solvent should preferably be non-corrosive to materials used in plant equipment to minimize capital and maintenance costs, and should be non-toxic, to minimize any dangers to plant personnel.

In leaching, usually the metallic values in an ore are selectively dissolved using a suitable liquid reagent. However, there are processes where the gangue minerals are first leached out leaving the valuable metals in the solid residue, which after separation, are leached again.

The selectivity in dissolution depends on the nature of the reagent while the rate of leaching depends on various factors including temperature, pressure, the vol. of the leaching liquid, the ore particle size, the composition and concentration of the reagent, the duration of the leaching reaction, and the degree of aeration of the leaching reagent.

2.2.2.3 Leaching Reagents

The common categories of the leaching reagents are water, acids, bases and aqueous solution.

The criteria for the selection of an effective reagent are as follows:

- Leaching by the reagent must be as selective and as rapid as possible.
- It should be possible to dissolve the reagent in order to prepare a sufficiently strong leaching solution which can ensure a fast rate of leaching.
- The reagent should preferably be non-corrosive to materials used in plant equipment to minimize capital and maintenance cost, and should be nontoxic to minimize any damage to plant personnel.
- The reagent should be economical and preferably allow regeneration.

During leaching, a mineral decomposes in an aqueous environment. The mineral may simply dissolve completely, leaving behind the gangue as a solid residue. Sometimes only some constituents of the mineral may dissolve. During alkali or acid leaching with or without additional reagents, a metal forms simple or complex ions.

Zinc fine blend were used for recovery of zinc. Figure 2.1 shows the process flow chart for the hydrometallurgical recovery of zinc from the fine blend using sulfuric acid as a leaching reagent. The produced leach liquor was either purified and electrowinned for producing a pure zinc metal.

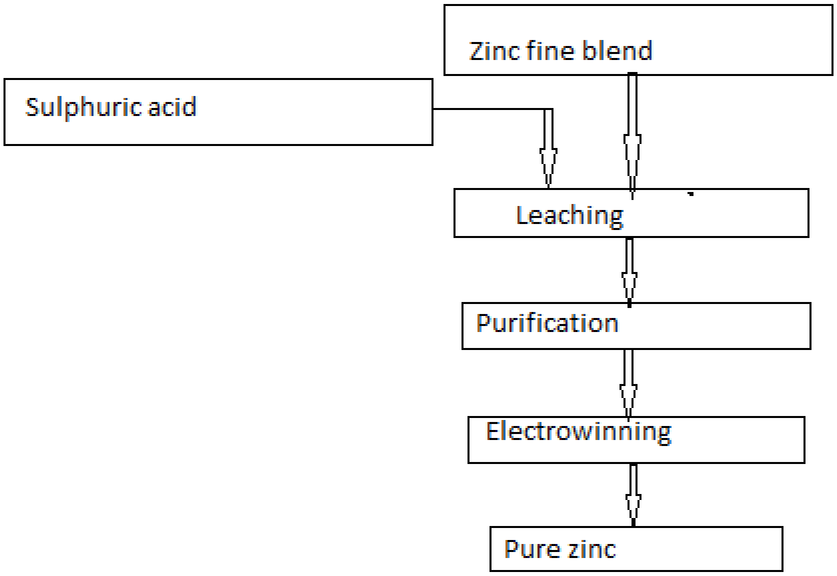


Fig. 2.1: Schematic of process flow sheet for hydrometallurgical recovery of zinc.

2.2.3 Rate of Reaction

Rates of reaction vary from those which seem to be instantaneous, e.g. reaction of H_3O^+(aq) with OH^-(aq), to those which are so slow that they appear not to occur, e.g. conversion of diamond to graphite. Intermediate situations range from the slow oxidation of iron (rusting) to a typical laboratory experiment such as the bromination of an alkene. But in all cases the product concentration shows a smooth increase with time, and the reaction rate describes how rapidly this increase occurs.

The reactant concentration remaining at various times is the fundamental quantity which requires measurement in any kinetic study.

2.2.3.1 Classification of Reaction Rates

Reactions are roughly classified as fast reactions and the slow reactions. The borderline is indistinct, but the general consensus is that a „fast" reaction is one which is over in one second or less. Reactions slower than this lie in the conventional range of rates, techniques can be adapted to measure rate. Fast reactions require special techniques.

A very rough general classification of rates can also be given in terms of the time taken for reaction to appear to be virtually complete, or in terms of half-lives.

Table 2.1: Types of reaction according to their rate [28].

Type of reaction	**Time span for apparent completion**	**Half-life**
very fast rate	microseconds or less	10^{-12} to 10^{-6} second
fast rate	Seconds	10^{-6} to 1 second
moderate rate	minutes or hours	1 to 10^{3} second
slow rate	weeks	10^{3} to 10^{6} second
very slow rate	weeks or years	$>10^{6}$ second

The half-life is the time taken for the concentration to drop to one-half of its value. If the concentration is 6×10^{-2} mol dm^{-3}, then the first half-life is the time taken for the concentration to fall to 3×10^{-2} mol dm^{-3}. The second half-life is the time taken for the concentration to fall from 3×10^{-2} mol dm^{-3} to 1.5×10^{-2} mol dm^{-3}, and so on.

The dependence of the half-life on concentration reflects the way in which the rate of reaction depends on concentration.

Care must be taken when using the half-life classification. First order reactions are the only ones where the half-life is independent of concentration.

2.2.3.2 Factors Affecting the Rate of Reaction

Several factors can affect the rate of a reaction. These are as follows:

- The standard variables are concentration of reactants, temperature and catalyst, inhibitor or any other substance which affects the rate.
- Chemical reactions are generally very sensitive to temperature and must be studied at constant temperature.
- Rates of reactions in solution and unimolecular reactions in the gas phase are dependent on pressure.
- Some gas phase chain reactions have rates which are affected by the surface of the reaction vessel. Heterogeneous catalysis occurs when a surface increases the rate of the reaction.
- Photochemical reactions occur under the influence of radiation. Conventional sources of radiation, and modern flash and laser photolysis techniques, are both extensively used.

- Change of solvent, permittivity, viscosity and ionic strength can all affect the rates of reactions in solution.

2.2.3.3 Common Experimental Features for All Reactions

There are some experimental factors which must be followed during the reaction if the kinetics of that reaction is to be followed. They are:

- Chemical reactions must be studied at constant temperature, with control accurate to $\pm 0.01^{o}C$ or preferably better. The reactants must be very rapidly brought to the experimental temperature at zero time so that reaction does not occur during this time.
- Mixing of the reactants must occur very much faster than reaction occurs.
- The start of the reaction must be pinpointed exactly and accurately. A stop-watch is adequate for timing conventional rates; for faster reactions electronic devices are used. If spectroscopic methods of analysis are used it is simple to have flashes at very short intervals, e.g. 10^{-6} s, while with lasers intervals of 10^{-12} s are common. Recent advances give intervals of 10^{-15} s.
- The method of analysis must be very much faster than the reaction itself, so that virtually no reaction will occur during the period of concentration determination.

2.2.3.4 Conventional Methods of Following a Reaction

Conventional methods determine directly changes in concentrations of reactants and products with time, but they may have the disadvantages of sampling and speed of analysis.

When reaction is sufficiently fast to result in significant reaction occurring during the time of sampling and analysis, the rate of reaction is slowed down by reducing the temperature of the sample drastically, called „quenching"; reaction rate generally decreases dramatically with decreasing temperature. Alternatively, reaction can be stopped by adding a reagent which will react with the remaining reactant. The amount of this added reagent can be found analytically, and this gives a measure of the amount of reactant remaining at the time of addition.

2.2.4 Interpretation of the Experimental Data

The first step in the analysis converts the experimental observations to plots of [reactant] versus time. Fig. 2.2 and 2.3 illustrate some typical data.

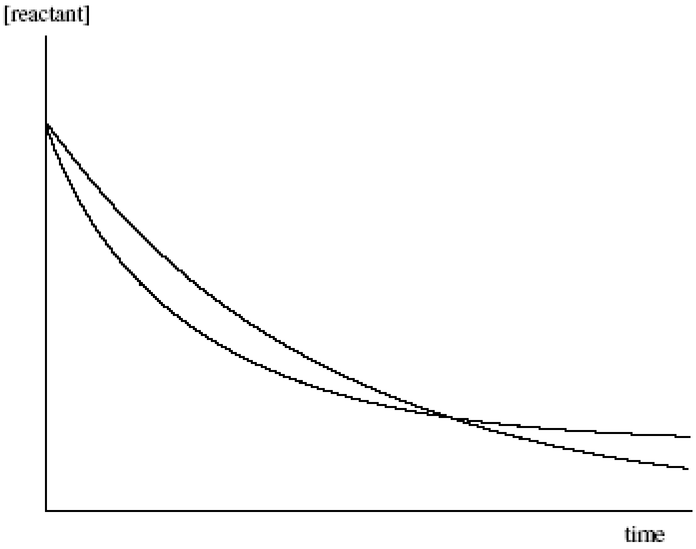


Fig. 2.2: Graphs of [reactant] versus time showing curvature [40]

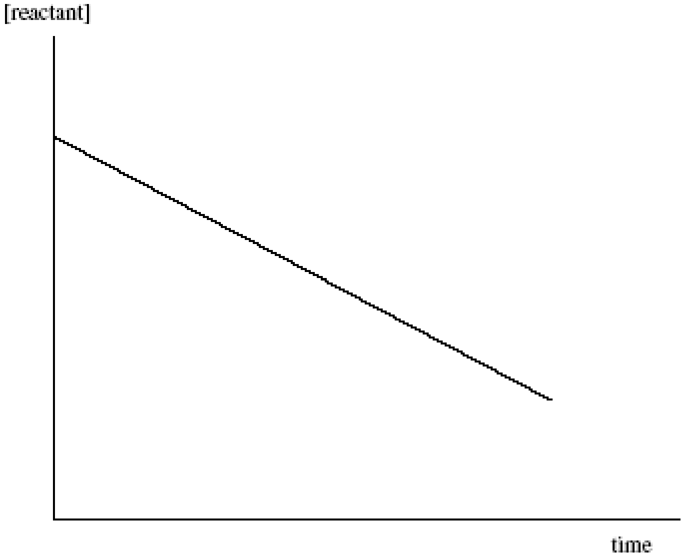


Fig. 2.3 Graph of [reactant] versus time showing linearity [40]

A simple qualitative description of how fast reaction occurs can be taken from a direct observation of how long it takes for a certain percentage reaction to occur. But in a quantitative analysis rate must be precisely defined, and once this has been done it becomes apparent how inadequate the loose definition of rate in terms of percentage reaction actually is.

The more precise meaning of the term rate of reaction, defined as how fast the [reactant] changes with time, can be illustrated on graphs of concentration versus time (Fig. 2.4(a), (b) and (c)). The average rate over the time interval t_1 to t_2 when the concentration decreases from c_1 to c_2 is specified by

$$\frac{c_2 - c_1}{t_2 - t_1} = gradient\ of\ line\ AB$$

However, this gives limited information. What is needed is the actual rate at a particular [reactant], called the „instantaneous rate". This corresponds to situations where $c_2 - c_1 \rightarrow 0$, and $t_2 - t_1 \rightarrow 0$, and describes the gradient of a tangent to the curve at the particular concentration or time, e.g. the gradient of line EF, Fig. 2.4(b), gives the instantaneous rate at c" and t". The gradient of EF is negative, but the rate of reaction is defined to be positive, and so the rate of reaction in terms of reactant = - the gradient. It is important to include the minus sign.

The initial rate is a very important quantity in kinetics, especially for complex reactions involving many steps where secondary reactions and products of reaction may affect the rate. The initial rate is the rate at the very start of reaction, Fig. 2.4(c), and, with the exception of chain reactions, is the line of steepest gradient giving the maximum rate.

The units of rate are given in terms of concentration per unit time or pressure per unit time, i.e. mol dm^{-3} $time^{-1}$; or N m^{-2} (or atm, mmHg) $time^{-1}$.

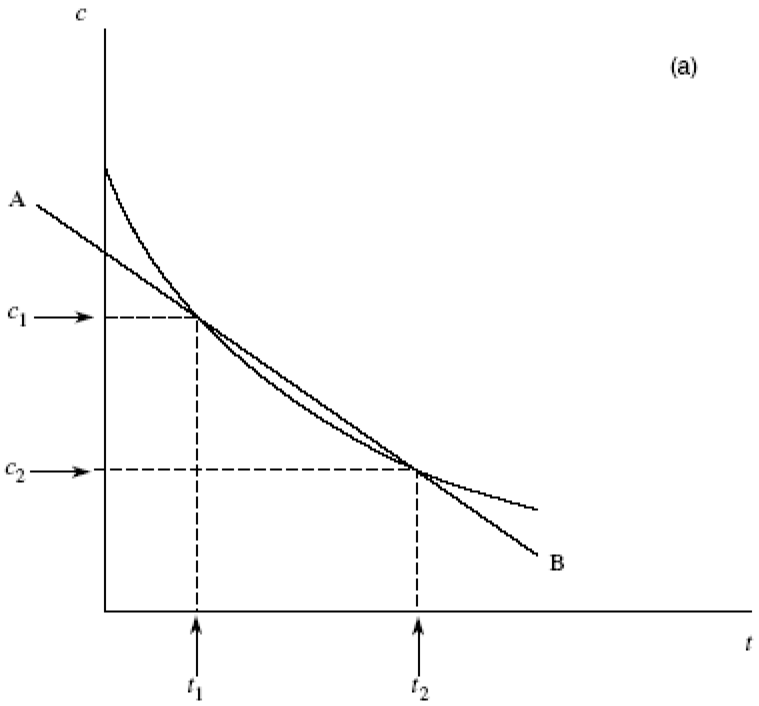


Fig. 2.4(a): Graph of concentration versus time, illustrating the meaning of average rate [28].

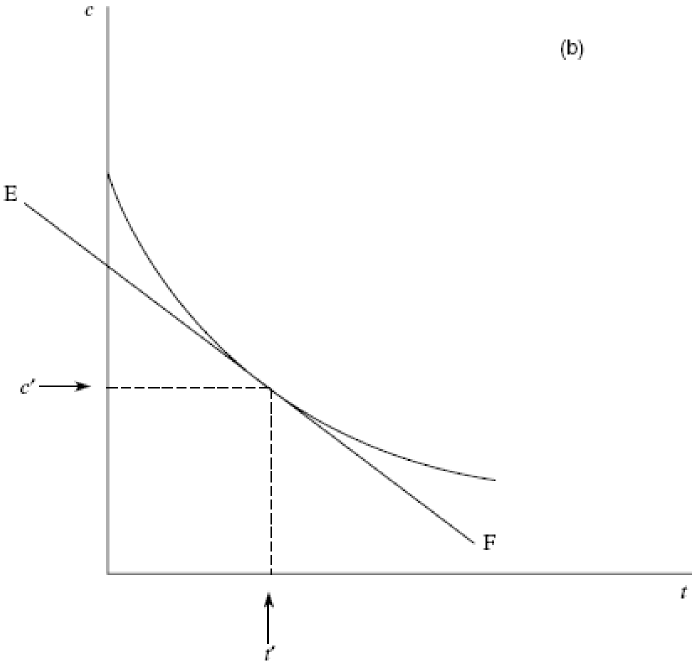


Fig. 2.4(b): Graph of concentration versus time, illustrating the meaning of instantaneous rate [28].

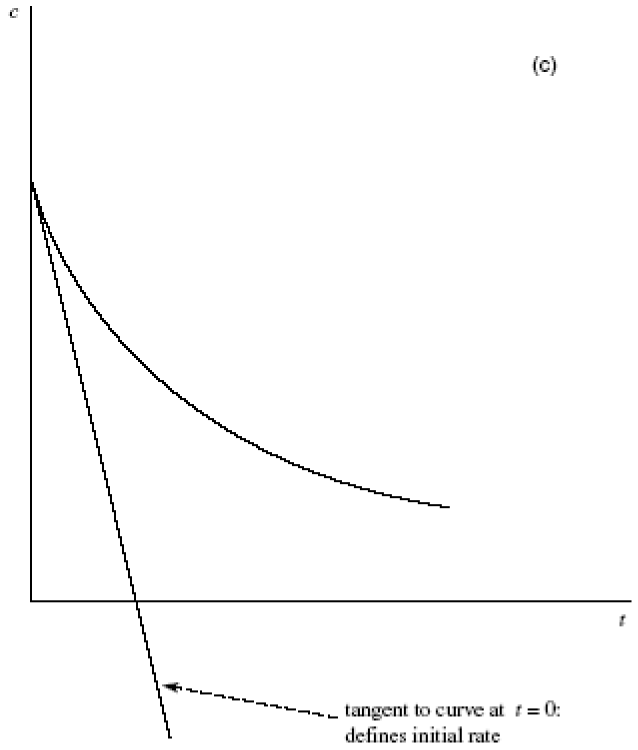


Fig. 2.4(c): Graph of concentration versus time, illustrating the meaning of initial rate [28].

2.2.4.1 Dependence of Rate on Concentration

In Fig. 2.5, three tangents have been drawn. The magnitudes of the gradients lie in the order AB > CD > EF and these are at points (t_1,c_1), (t_2,c_2) and (t_3,c_3) respectively, i.e. as [reactant] decreases so does the rate.

The conclusion follows that the rate depends in somehow on [reactant] remaining, i.e.

$$\text{Rate} \infty [\text{reactant}]^n$$

where n is a number which states exactly how the rate depends on the [reactant]. It is called the order. From this,

$$\text{Rate} = k\,[\text{reactant}]^n$$

where k is a constant of proportionality called the rate constant.

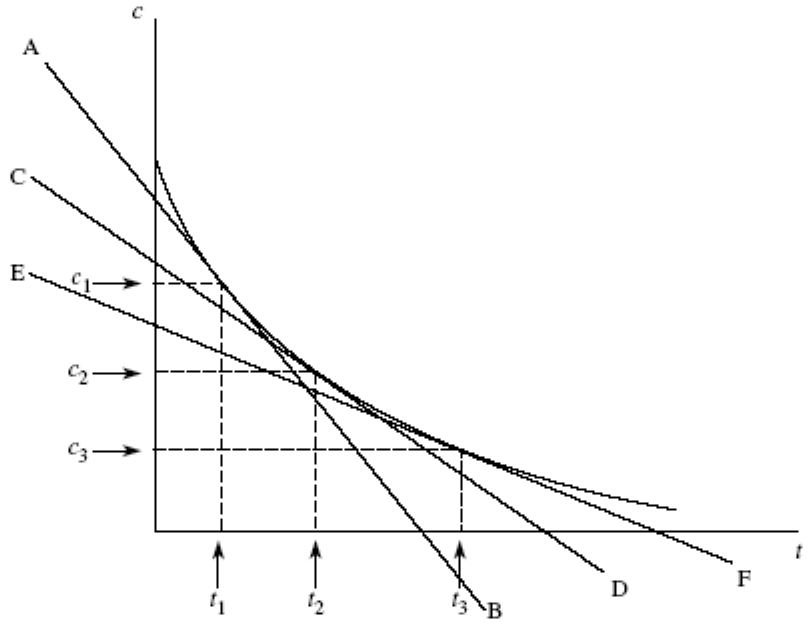


Fig. 2.5: Graph of concentration versus time, illustrating the dependence of rate on [reactant] [28].

- If n = 1, the reaction is first order;
- if n = 2 the reaction is second order.
- If n = 3/2, the reaction is three-halves order;
- if n = 0, it is zero order.

If the reaction involves two substances A and B and

Rate = k [A][B]

then the order is first with respect to A and first with respect to B, with the reaction being second order overall.

Likewise, if

Rate = k $[P]^2[Q]$

then the reaction is second order in P, first order in Q and third order overall.

The equations

Rate= k $[\text{reactant}]^n$

Rate = k $[\text{reactant}_1]^m[\text{reactant}_2]^n$

are called the rate expression, or the rate equation. In general if the rate of reaction depends on the concentrations of several species, then

$$\text{Rate} = k\,[P]^m[Q]^n$$

and a kinetic analysis aims to find the value of m, n and k at constant temperature for the reaction being studied.

Sometimes the dependency of reaction rate on the concentration of leaching reagent is presented with empirical relationships that vary from one leaching system to others [41].

2.4.2 Meaning of the Rate Expression

There are several meaning of the rate expressions. They are:

1. rate = k [reactant] describes a first order reaction where
    - if the concentration increases by a factor of two, the rate also increases by a factor of two,
    - if the concentration increases by a factor of six, the rate also increases by a factor of six.
2. rate = k $[\text{reactant}]^2$ describes a second order reaction where
    - if the concentration increases by a factor of two, the rate increases by a factor of 2^2, i.e. four,
    - if the concentration increases by a factor of six, the rate increases by a factor of 6^2, i.e. 36.
3. rate = $k[\text{reactant}]^0 = k$ describes a zero order reaction where
    - no matter how the concentration varies, the rate remains constant.

2.2.5 Temperature Effect on Reaction Rate

Chemical reaction rates increase with an increase in temperature because at a higher temperature, a larger fraction of reactant molecules possesses energy in excess of the reaction energy barrier. The relationship between the rate constant k of an elementary reaction and the absolute temperature T is the Arrhenius equation.

$$k = A.\ \exp(-E_A/RT)$$

A is called the Arrhenius factor and E_A is the activation energy [42-48].

2.2.5.1 Activation Energy

The activation energy of a reaction is the amount of energy needed to start the reaction. It represents the minimum energy needed to form an activated complex during a collision between reactants. All the particles in a system do not undergo transformation at one and the same time. Reactants and products coexists throughout the transformation and at any instant only a small fraction of the available particles can be in the process of transformation for the simple reason that only a fraction of the particles have free energy in excess of the mean and therefore, energetically suitable for transformation. It is always possible to find more than one set of configurational changes capable of providing a given transformation. Called „reaction paths" each of these is associated with a free energy curve similar to that shown in Fig. 2.6. However, because different transition configurations are involved, the activation energies are different.

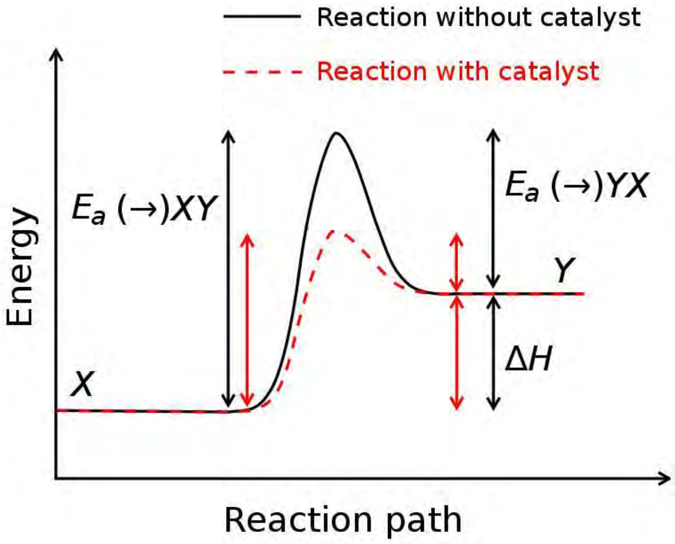


Fig. 2.6: Energy versus reaction coordinate diagram to explain activation energy [49].

The free energy of an atom or group of atoms during transformation first increases to a maximum and then decreases to the final value. The configuration associated with the maximum in the free energy curve is assumed to be the transition or activation state. Only those with excess free energy equal to or greater than E_A, called activation energy, will transform. Those with insufficient free energy must wait until they receive the necessary activation energy from thermal fluctuations. The process is termed thermal activation.

2.2.5.2 Evaluation of Activation Energy

Activation energy E can be obtained using either a conventional integral approach or differential approaches.

If the integrated form of the kinetic law for a reaction g(α) {g(α) = kt, where k is rate constant)} is known then one can plot, for different isothermal experiments, values of g(α) against time (Fig. 2.8). Each of these plots will be linear, the slope being the value of k at that temperature. Since, k=A exp(-E/RT), where A is Arrhenius constant, the plot of ln k versus reciprocal of temperature (Fig. 2.9) would be a straight line [42]. The slope of such a line gives –E/R and intercept ln A. Such an approach requires prior knowledge of the form of the function g(α). There is also an implicit assumption that the activation energy does not change during the course of reaction. A typical reaction and its associated concentration or degree of reaction versus time plot is shown in Fig 2.7 [30].

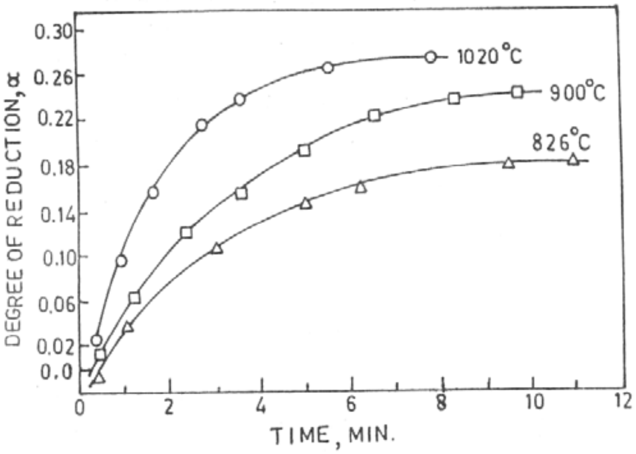


Fig. 2.7: Typical plot of degree of reaction versus time (Kinetic data for isothermal reduction of iron ore [44].

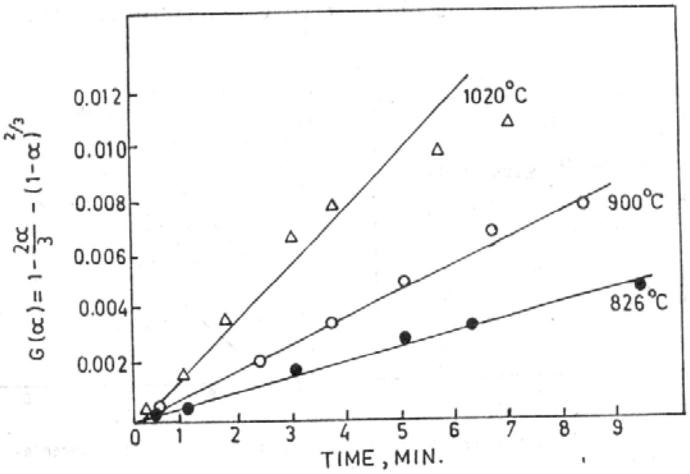


Fig. 2.8: Ginstling-Brounshtein plots to linerize data [44].

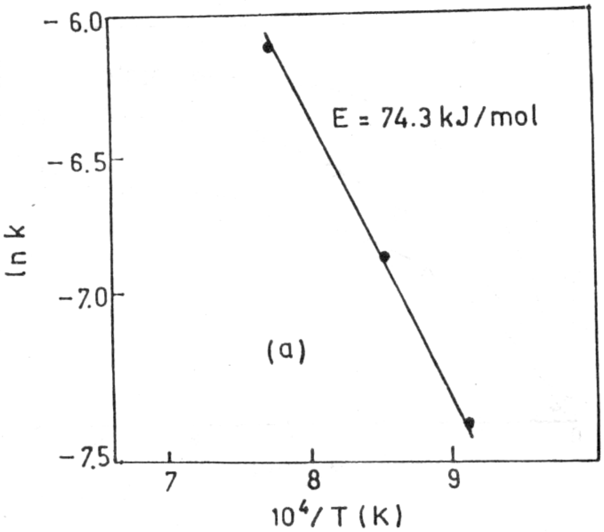


Fig. 2.9: Arrhenius plot for rate constant values [44].

In the differential approach it is not necessary to assume any kinetic law at all. One can evaluate the activation energy E without knowing the forms of g(α).

We know that the rate of a reaction $\frac{dC}{dt} = k.f(C) = A.\exp(-E/RT).f(C)$

Considering a fixed value of concentration of reactant C one obtains

$$\ln\left(\frac{dC}{dt}\right)_C = \ln A + \ln f(C) - E/RT$$

Since f(C) has a fixed value for a fixed C, it follows that a plot of the left hand side of the above equation against reciprocal temperature would be a straight line, the slope of which should yield the value of E/R (Fig. 2.10) [42].

In this approach one has the advantage that it is not necessary to know the form of either g(α) or f(C). Also, one does not assume E to be independent of C, and therefore, E can be calculated at different levels of C. However, the disadvantage is that one has to know (dC/dt) values. One can obtain these from C-t plots but calculation of slopes involves uncertainties.

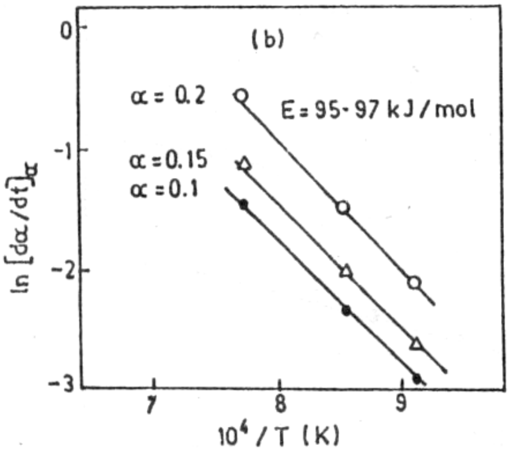


Fig. 2.10: Plots of $\ln(d\alpha/dt)_\alpha$ against 1/T for three levels of concentration [44].

Sometimes activation energy of the different stages of a reaction can be different [46]. So, in that case, determination of activation energy of the rate determining stage is important.

2.2.6 Purification

Purification removes the impurity metals that dissolved with the zinc during leaching. The principal ones found in ash are Fe, Pb, Cu, Sn, Al, Cl, Si, Mn, Mg, Ni, Cd, Si, Cr, etc. If these impurities remain, not only will the zinc produced from the subsequent electrolysis be insufficiently pure, but their presence will interfere with the smooth running of the electrolysis process itself. Among these impurities, for chlorine removal, two methods may be followed, such as washing with distilled water and calcination. Other impurities can be removed by precipitation and cementation techniques after dissolution of the sample in leaching reagent [6-12].

Iron goes into the solution mostly as Fe^{2+} during leaching. For precipitation of iron, Fe^{2+} should be converted into Fe^{3+} by oxidation. After oxidation, Fe^{3+} can be precipitated by controlling the P^H between 4.5 and 5.2.

Other impurities can be removed by cementation technique. As zinc is a highly reactive metal compared to impurity elements, when pure zinc is added to the solution, zinc will be oxidized and dissolves, with the opposite side of the reaction being the reduction of the other dissolved metals back to their metallic state as follows:

$M^{2+} + Zn = Zn^{2+} + M$

Thus other impurities in their metallic form can be separated from leach liquor by filtration.

2.2.6.1 Qualitative Analysis of Metal Ions in Solution [51]

It is extremely useful to know how to detect the presence of specific ions in an aqueous solution. This type of analysis falls under the general category of analytical chemistry called qualitative analysis, which addresses the question "What is in a sample?" The basis for a qualitative analysis is the fact that ions will undergo specific chemical reactions with certain reagents to yield observable products. For example, silver ion can be precipitated with hydrochloric acid to yield solid silver chloride. Because many cations will not react with hydrochloric acid in this way, this simple reaction can be used to separate ions that form insoluble chlorides from those that do not. In fact, the qualitative detection of ions in a mixture is commonly accomplished by a system of analysis in which precipitation reactions play a major role. In addition, acid-base reactions, oxidation-reduction reactions, and the formation of complex ions are often used in a systematic way for either separating ions or for determining the presence of specific ions.

The qualitative analysis of ions in a mixture must follow a scheme that can be summarized as follows: (1) Add reagents that exploit the more general properties of ions to separate major groups of ions; (2) separate major groups into subgroups with reactions that will distinguish less general properties; and (3) add reagents that will specifically confirm the presence of individual ions. Following this general three-step plan, several different analytical schemes have been devised that are based on various ways of defining major groups. In this course, you will follow a scheme which separates cations into five major groups according to them solubilities of their compounds:

Group I (Ag^+, Pb^{2+}, Hg^{2+}) cations produce insoluble chlorides so they can be precipitated with dilute HCl, while all other cations remain in solution.

Group II (Cu^{2+}, Bi^{3+}, Cd^{2+}, Hg^{2+}, As^{3+}, Sb^{3+}, Sn^{4+}) cations produce very insoluble sulfides (K_{sp} values less than 10-30) so they can be precipitated by low amounts of sulfide ion; this can be achieved by adding an acidic solution of H_2S.

Group III (Al^{3+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Mn^{2+}) cations produce slightly soluble sulfides (Ksp values more than 10-20) so they can be precipitated by relatively high amounts of sulfide ion; this can be achieved by adding a basic solution of H_2S.

Group IV (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) cations, as well as all of the above groups, produce insoluble carbonates so they can be precipitated by the addition of carbonate once the ions of the first three groups have been removed.

Group V (Na^+, K^+, $NH4^+$) cations do not precipitate with any of the above reagents.

For a successful qualitative analysis based on the above five groups, the order of reagent addition is crucial and should follow the order listed above (that is, group I first, group II second and so on). For example, addition of carbonate first would precipitate everything but the group V ions or addition of basic H2S first would precipitate all group II and group III ions.

A. Group I Analysis: Pb^{2+}, Hg_2^{2+}, Ag^+

Chemistry of the Precipitation of the Group I Cations

The precipitating reagent of Group I is a dilute solution of hydrochloric acid, and the ions precipitated are those of silver, Ag^+, mercury (I), Hg_2^{2+}, and lead (II), $Pb^{2+.}$ The net ionic equations are:

$Ag^+ + Cl^- \rightarrow AgCl(s)$ (AgCl is white, turning purple in light)

$Hg_2^{2+} + 2Cl^- \rightarrow Hg_2Cl_2(s)$ (Hg_2Cl_2 is white)

$Pb^{2+} + 2Cl^- \rightarrow PbCl_2(s)$ ($PbCl_2$ is white)

B. Group II Analysis: Pb^{2+}, Bi^{3+}, Cu^{2+}

Chemistry of the Precipitation of the Group II Cations

The ions of Groups II and Groups III are separated by precipitation of their insoluble sulfides. The ions of Group II are precipitated as their sulfides from an acidic solution of hydrogen sulfide, and for this reason Group II is often called the Acid Hydrogen Sulfide Group. The ions of Group III are precipitated as their sulfides from a basic solution of hydrogen sulfide, and Group III is often called the Basic Hydrogen Sulfide Group. If the hydrogen ion concentration is maintained in the range of 0.1 M and 0.3 M, (pH=0.5-1.0) the ions of Group II will precipitate, but not the ions of Group III, the sulfides of which are more soluble.

The reactions involved in the precipitation of Group II are as follows (for the ions we are considering):

$Pb^{+2} + H_2S \rightarrow PbS(s) + 2H^+$ (PbS is black)

$2Bi^{+3} + 3H_2S \rightarrow Bi_2S_3(s) + 6H^+$ (Bi2S3 is brown)

$Cu^{+2} + H_2S \rightarrow CuS(s) + 2H^+$ (CuS is black)

C. Group III Analysis: Ni^{2+}, Al^{3+}, Cr^{3+}

The Chemistry of the Precipitation of the Group III Cations

The ions of Group III are precipitated as their sulfides, or as their hydroxides, from a basic solution of hydrogen sulfide. The sulfides of the ions of Group III are not sufficiently insoluble to be precipitated in the acidic solution of hydrogen sulfide of Group II but will be precipitated by basic solutions of hydrogen sulfide.

A basic hydrogen sulfide solution also contains a concentration of hydroxide ions. Although this is very small, it is sufficient to precipitate the very insoluble hydroxides of aluminum and chromium (III) ions. The equations for the precipitation of the ions of Group III under consideration in our laboratory work are:

$Ni_{2+} + H_2S \rightarrow NiS(s) + 2H^+$ (NiS is black)

$Al^{3+} + 3NH_3 + 3H^2O \rightarrow Al(OH)_3$ (s) + $3NH^{4+}$ (Al(OH) 3 is white, gelatinous)

$Cr^{3+} + 3NH_3 + 3H_2O \rightarrow Cr(OH)_3$ (s) + $3NH^{4+}$ (Cr(OH) 3 is gray-green, gelatinous)

Care must be taken not to have the solution of hydrogen sulfide too basic, for if the concentration of hydroxide ion is sufficiently high, unwanted precipitation of magnesium hydroxide will take place. To achieve a hydroxide ion concentration of the necessary concentration (about 1×10^{-5}M) an ammonia-ammonium chloride buffer is produced by adding ammonia to a solution of ammonium chloride.

2.2.7 Electrowinning

In electrowinning processes the metal is usually in solution in the electrolyte from which it is deposited onto the cathode, the anode being an insoluble conductor.

This process is important for the very reactive light metals: aluminum and magnesium, which almost exclusively are produced by electrolysis of fused salts. For other metals such as copper and zinc, electrowinning from aqueous solutions represents an alternative to pyrometallurgical process. Electrowinning with aqueous electrolytes or fused salts is important for the production of high purity copper, zinc and aluminum.

One advantage of using electrical energy to drive chemical reactions is that this electron fuel does not introduce unwanted impurities into the cell.

2.2.7.1 The Electrochemical Cell

Electrolysis consists of two separate and equivalent chemical reactions. At the Anode, oxidation takes place (i.e.; electrons are produced) and at the cathode reduction (i.e.; electrons are consumed) takes place (Fig. 2.11). Such a reaction involving the transfer of electrons cannot be carried out in isolation.

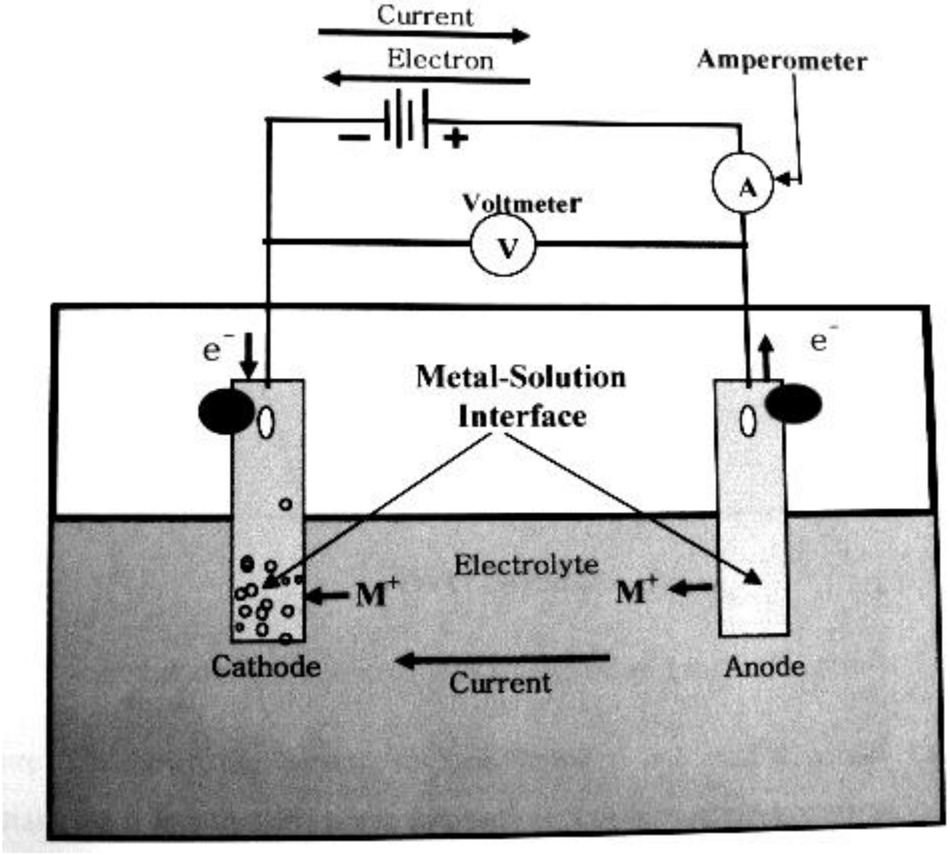


Fig. 2.11: Schematics of an electrolytic cell.

If the reaction results in the consumption of electrons then for the reaction to continue these electrons, which are the essential reactants, must be supplied by some other reaction. These complementary reactions then make up the electrochemical cell.

2.2.7.2 The Electrodes

The electrodes employed in electrochemical processes may be solid, particulate or liquid. The electrodes may be actually involved in chemical reactions, being consumed or deposited from the solution, or it may remain inert merely providing an interface at which the reactions may occur.

The following three properties are essential to all types of electrodes if the power requirements of the process are to be minimized

(i) The material should be a good conductor
(ii) The activation over-voltage of the electrode should be low
(iii) The electrode should not become passivated during the cell operation, that is, they should not react to form on the electrode surface, any compound which does not promote the desired electrochemical reaction.

In the case of solid electrodes there are additional features which are necessary to obtain satisfactory cell performance.

(i) The electrode should be easily manufactured or prepared
(ii) They should resist corrosion by elements in the cell
(iii) They should have good dimensional stability, strength and resistance to abrasion
(iv) Should be of low cost.

Electrolysis may be carried out with either insoluble or soluble anodes. The former method is exemplified in the recovery or electrowinning of copper from solutions obtained from the leaching of ores: the second type by the electrolytic refining of a metal such as copper, silver, or gold. Using the symbol e as a single electron, we may write for the reaction at a cathode
$Cu^{2+} + 2\ (e) \rightarrow Cu$
With an insoluble anode, the reaction is $2SO4^{2-} + 2H_2O - 4(e) \rightarrow 2H_2SO_4 + O_2$
Making the reaction for the cell
$2CuSO_4 + 2H_2O \rightarrow 2Cu + O_2 + 2H_2SO_4$

2.2.7.3 Electrolyte

In electrolytic operations, the selection of a proper electrolyte is the most important requirement. In most electrochemical cells used in extractive metallurgy the electrolytes are in the liquid state. Solid electrolytes are commonly used in battery manufacture but in some cases may also be used as semi-permeable membranes in production cells. The basic conditions that an electrolyte must satisfy are:

1. It must have a sufficiently high ionic conductivity, and conduction must be entirely due to ions. (Any electronic contribution to the total conduction would short-circuit the electrodes and lead to a wastage of electricity.)
2. It must be chemically inert towards the electrodes, the container material, and the electrolysis products.
3. It must be stable at the temperature of operation.
4. When a solution containing the metal to be extracted is being used, then it must be chemically more stable than the solute, (i.e., the metal compound should dissociate at a voltage appreciably lower than that required for the dissociation of the solvent.)

The major charge carriers in electrolytes are, by definition, ions rather than electrons. The lower conductivity of the solution the higher is the resistance within the electrical circuit of externally driven cells this obviously leads to the need for increased applied potentials to achieve a given current density and hence increased power consumption. In self driven reasons any resistance to electron or ion flow will tend to reduce the corrosion current density that can be obtained in the system.

It is essential that the electrolyte does not decompose in the cell during operation. Decomposition of the electrolyte will lead to increased running costs due to material replacement. Moreover, the current efficiency of the cell will be reduced and the purity of the product will be affected in general, therefore, the electrolyte material must be more stable than the products of the cell.
The rates of electrochemical reactions are often limited by mass transport of the ions in the electrolyte. The driving force for the transport of the ions to and from the reaction interface and the bulk solution is determined by the difference in the activities or concentrations of the species. Therefore, to obtain high production rates it is necessary that the solubility of the reactant ionic species in the electrolyte is high.

Electrolytic dissociation of ionic media is governed by two laws which were enunciated by Michael Faraday are as follows [8,19,20]:

(i) The quantity of material deposited at an electrode is directly proportional to the quantity of electricity passed through the electrolyte.

(ii) The quantity of material deposited at an electrode is proportional to the equivalent weight of the same. In other works, the same quantity of electricity will release the same number of gram equivalent of a substance.

The electrochemical equivalent of a substance is defined as the number of grams of that substance released by 1 coulomb of electricity, i.e., by current of 1 ampere during its passage for a duration of 1 second. Chemical equivalent weight is atomic weight divided by its valency. Thus the chemical equivalent is proportional to the electrochemical equivalent. This proportionality factor (Faraday"s Constant) was first determined from experimental results on electrodeposition of silver.

The amount of deposition can be calculated from Faraday"s Law

$$W = \frac{MIt}{nF} \times \beta$$

2.2.7.4 Current Efficiency [8,19,20]

Faraday"s law of electrolysis states that the quantities of substances set free at the electrodes are directly proportional to the quantity of electricity which passes through the solution. It may so happen that some current passing is not used in carrying out deposition of the valuable metal. The current efficiency may be defined as the ratio between the amount of metal actually deposited and that called for by Faraday"s law, for example, if in an electrolytic tank 26.5 pounds of copper are deposited in a certain time, the current efficiency is

$$\frac{26.5}{28.4} \times 100 = 93.2\%$$

where 28.4 is the amount which should theoretically be deposited

The apparent loss of current may be due to one or more of several reasons. It could be due to mechanical losses at the electrodes. If the temperature of operation is close to the boiling point of the concerned metal, then some metal may be lost by vaporization. Occasionally the metal liberated by electrolysis is re-dissolved in the electrolyte or reacts with it Passage of electricity can bring about unwanted dissociation reactions often called „side reactions". Current efficiency may also take into account loss due to some current not passing through the electrolyte. For example, the total current may be measured by ammeters placed in the mainline and the theoretical deposit calculated from this amount. Some of the current, however, may not pass through the electrolyte at all or may leak away through other conductors.

2.2.7.5 Voltage Requirements [8,19,20]

The energy consumed per unit time during electrolysis is given by the product $I \times V$ where I is current, and V is voltage across the cell. Since the current is directly related to output of metal, the energy consumption in electrolytic production of metal can be minimized through either of the following:

1. Maximization of the current efficiency.
2. Minimization of the voltage requirement consistent with other requirements.

The total voltage requirement for the electrolytic cell may be expressed as a sum of several terms. $V_A = V_D + V_R + V_O + V_E$

Where,

V_A = Voltage applied across the cell

V_D = Thermodynamic voltage requirement for the overall reaction (decomposition voltage)

V_R = Ohmic voltage drop due to resistance of the electrolyte

V_O = Sum of the over-voltages for cathode and anode (η_c and η_a respectively)

V_E = Voltage drop due to electronic resistance in the circuit (electrodes, contact points etc)

With the exception of V_D, all the factors in the right hand side of Equation depend on the current density I. The higher the value of I, the higher are the values of V_R, V_O, and V_E.

2.2.7.6 Decomposition Voltage [8,19,20]

During electrolysis, the reactions take place at two distinct regions: the cathode and the anode. The overall cell reaction is a summation of the reactions at the two electrodes. The decomposition voltage is the difference between the reversible potentials for the anode and the cathode reactions.

The thermodynamic voltage requirement for the cell reaction (V_D) is related to the free energy-change for the overall cell reaction,

$\Delta G = -zFV_D$

If reactants and products are at their standard states $\Delta G = \Delta G^o$ and $V_D = V^o$. V_D is the difference of the single electrode potentials of the cathode and the anode.

A typical current-voltage curve for electrolytic dissociation of a solute dissolved in a solution is hour, in Fig 2.12. No appreciable current flows through the cell until the voltage reaches a certain value. Beyond that the current rises rapidly. Very small initial currents are known as residual currents that are generally larger for fused salts than for aqueous solutions.

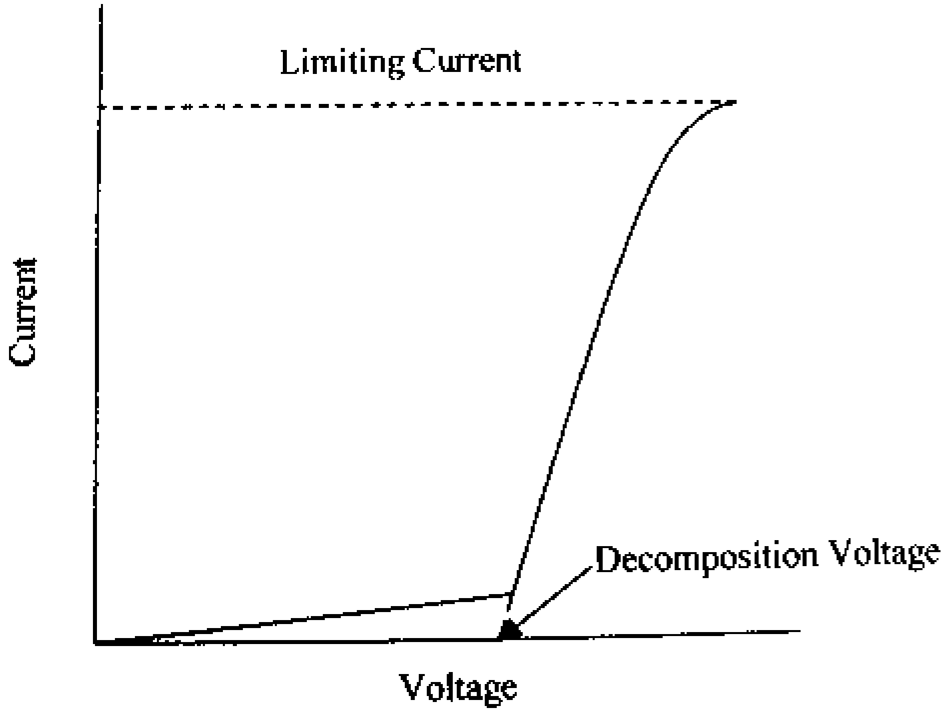


Fig. 2.12: Current-voltage Relationship during Decomposition of an Electrolyte.

The minimum voltage at which appreciable current starts to flow is called the decomposition voltage and it should be equal to V_D under ideal conditions. This voltage indicates the onset of sustained decomposition of an electrolyte or of a particular solute in the electrolyte. Beyond the decomposition voltage, current increases appreciably with increase in the applied voltage. The current increase, however, does not continue indefinitely. Beyond a certain voltage, the current levels off to a constant value known as the limiting current. The limiting current depends among other factors, directly on the surface area of the electrode. The maximum current that can be drawn per unit area of an electrode is known as the limiting current density (i_d) electrode.

2.2.7.7 Overvoltage [8,19,20]

The decomposition voltage of an electrolyte varies with the nature of the electrodes used in the electrolysis; higher voltage is required to decompose sulfuric acid between a platinum anode and a lead cathode than between two platinum electrodes. This can be attributed to the extra work required to liberate hydrogen form a lead surface. The difference between the decomposition voltage and the equilibrium value for the electrodes question is called the overvoltage of the electrode.

2.2.7.8 Arrangement of Electrodes in Electrolytic Cell

The limiting current in the electrolytic cell and, therefore, the rate of production is limited by the surfaced area of the electrodes. It is, therefore, necessary to maximize the surface area if the production is to be maximized. Since it is not convenient to use very large electrodes, the surface area is increased by incorporating into the cell a large number of electrodes of convenient size. In a typical case of electro winning of copper, a rectangular electrolytic tank may contain 20-40 cathodes and anodes, the size of tank being approximately 4m x 1m x 1m. The electrodes are spaced as closely as practicable, so that the electrolytic resistance is the minimum. Arrangements are made so that all the anodes or cathodes in a given tank may be removed in a group, usually by means of an overhead crane.

There are two different systems of electrolytic refining. In first, the multiple system, the anodes and cathodes are connection multiple between two heavy bus bars which run along the side iof the electrolytic tank. In the second, the series system, the electrodes are connected in series and only the two end electrodes with the main bus bar or power line; the remainders are intermediate ones.

In the multiple systems, the tanks are of wood about 11 feet long feet wide, feet deep and lined with hard lead. Each contains thirty anodes and thirty-one cathodes.

In series system, the electrodes (they may cast but are usually rolled) are placed vertically in a tank, one electrode being connected to the positive conductor, the other to negative one. They are usually 3.5 to 4.0 feet long, 10 to 12 inches wide, and 0.5 to 3.5 inches thick, with an electrode spacing of inch as compared to 1 inch in the multiple system.

2.2.7.9 Electrowinning of Zinc from Aqueous Solutions

About 80 percent of world primary zinc production is derived via electrowinning. Zinc sulphide deposits are roasted to zinc oxide and then leached with spent electrolyte return from electrowinning. As already mentioned the high hydrogen overvoltage on zinc or aluminum cathodes makes it possible to deposit zinc from an acid solution. Succcessful zinc electrolysis depends up on the maintenance of the hydrogen overvoltage at the proper value and anything that lowers this value may have catastrophic results.

The presence of certain impurities in solution, even at extremely low concentration, can decrease the hydrogen overvoltage so such that zinc deposition may stop altogether. It may even bring about extensive resolution of zinc already deposited. Antimony, arsenic and germanium are particularly harmful in the respect but the additional presence of cobalt or nickel worsens the situation. The solution from the leaching plant, therefore, has to be purified extensively.

The morphology of the zinc deposit also affects the hydrogen over-voltage. In general a smooth zinc surface tends to maximize the hydrogen over-voltage.

Consequently the additions of reagents that promote a leveling action are beneficial to current efficiency. Various organic additions including animal glues have been shown to be effective. They inhibit the formation of dendrites and produce fine-grained deposits.

Following purification the strong zinc sulphate solution is passed into the electrolytic cell. The purified solution from the zinc leaching is neutral when it first enters the tank house, but it blends with electrolyte containing free acid and more acid is generated as electrolysis proceeds.

The electrolytic cell consists of alternate plate anodes and cathodes (approximately 1m x 1.6m x 0.07m). The cathodes are made of hard rolled aluminum. The anodes are made from lead 0.75 percent Ag alloy, are inert and provide a surface for the formation of O_2 gas through the reaction

$$2H_2O = O_2(g) + 4H^+ (aq) + 4e \qquad E^o = 1.228V$$

The electrodes can be arranged in electrically parallel or series circuits. Each cell consists, of 50-100 anode/cathode pairs. The centre to centre spacing between cathodes is approximately 0.1m. The use of aluminum starter sheets means that the cathode is perfectly flat and undistorted. This then ensures a constant anode/cathode spacing and hence a uniform current density over the whole of the cathode surface. Zinc is deposited on aluminum via the cathode reaction.

$Zn^{2}+ (aq) + 2e = Zn (c); E^{o} = 0.7V$

Every 2 or 3 days the zinc product is stripped from the aluminum sheets. The electrolysis is carried to the point where about half the zinc content is deposited and the acid content of the electrolyte has increased to 100g H_2SO_4 per liter. The solution is returned to the leaching plant.

2.3 Summary of Previous Work

Some investigator observed the phenomenon of the removal of chlorine by calcinations [2,3] or by washing with distilled water [4-6], as a little amount of chlorine is extremely harmful for electrolysis process. Investigation on recycling of zinc galvanizing ash has shown that zinc can be and is recycled from this discarded ash by both pyrometallurgical [7] and hydrometallurgical [8-10] processes. Hydrometallurgical methods are comparatively clean and can be adapted in small and medium scale industries. Some investigated hydrometallurgical processing by using sulfuric acid or by using hydrochloric acid as leaching agent. The main concern of hydrometallurgical process is the optimization of leaching parameters such as particle size, acid concentration, solid:liquid ratio, leaching time, and temperature [8,12]. These parameters were studied for leaching of galvanizing fine blend, galvanizing ash, galvanizing waste, flue dusts, low-grade zinc silicate ore to obtain maximum amount of zinc in solution. After leaching, leach liquor is purified [16-18] and pure zinc is obtained by electrowinning [18-20] of the purified leach liquor.

Thorsen et al. [10] developed a process for zinc and/or zinc sulfate recovery from zinc ash skimmed from galvanizing baths, flue dusts of zinc smelting, and Waelz processes. A liquid organic phase containing a cation exchanger (the commercial carboxylic acid Versatic 911) was efficient for zinc extraction from the leach liquor. Concentrated sulfuric acid was used for stripping of zinc, as sulfate, from the organic phase. Several sulfuric acid leaching processes have been investigated to recover zinc selectively from waste materials such as bughouse dust in iron and steel making, or from ash of galvanization process [22-26]. The leaching steps were carried out by hot concentrated sulfuric acid so as to generate dissolved zinc sulfate and precipitation of iron with other insoluble impurities.

Zinc was recovered from leach solutions as a pure zinc sulfate by vaporization and crystallization, or precipitated as basic zinc carbonate [26]. Zinc plant residue was blended with sulfuric acid and subjected to roasting, water leaching, and finally NaCl leaching [27]. Saleh and Hassan [28] studied the recovery of zinc from blast-furnace dust by roasting followed by leaching with ammonium sulfate.

Zinc can be electrodeposited from acid baths including Sulfate and chloride [30, 31]. The sulfate electrolysis has grown steadily to be the most widely applied method of zinc extraction today. Zinc is recovered from sulfate electrolyte by an electrowinning process in which zinc is electrodeposited on aluminum cathodes while oxygen is evolved at lead anodes. Saba and El-Sherief [20] reported that the minimum zinc concentration at which electrowinning should be stopped is around 40 g/L. The negative effects of impurities on the electrowinning of zinc from acid sulfate electrolytes were studied by many investigators in recent years [33-34]. Organic additives such as glue, gum Arabic, and gelatin are usually added to the electrolytic bath to counteract the harmful effects of metallic impurities. They improve cathode zinc quality for deposits from solutions containing various amounts of impurity.

Afifi et al. [33] showed that gelatin has an improving effect on the current efficiency and cathode zinc quality, the best choice of concentration is in the range of 2-5 mg/L, Zinc electrowinning is very sensitive to the presence of impurities in the electrolyte. Electropositive ions co-deposit on cathode zinc and make the product impure. The purification process of zinc electrolyte has been studied by many authors [35-39].

It would appear that any suspect impurity would, like cobalt, be deposited progressively on the zinc cathode. Its concentration in the solution would therefore decrease with time. As a consequence, if the electrolyte (with adjustment for concentration changes) were used with a fresh cathode for a second and a third time, increases in current efficiency could be expected. The bulk solutions were used repeatedly without improvement or deterioration [40].

In the electrodeposition of zinc from acidified zinc sulphate solutions the loss in current efficiency (CE) due to evolution of hydrogen at the cathode has often been attributed to the presence of metal impurities, and it has been thought that in a pure solution the CE would be 100%. Whatever the degree of purity achieved, hydrogen must always be produced simultaneously with zinc. At the start of electrolysis the CE is determined solely by the zinc/acid ratio, but when impurities are present the CE falls progressively as electrodeposition proceeds. Further, colloid silica which is always present in plant solutions is not responsible for the CE falling below 100%, nor are the lead anodes that are used in practice. There are some effects of manganese, both at the anode and the cathode, are reported. There is a deleterious influence of cobalt and manganese together on current efficiency [40].

2.4 Scope of Present Work

The leaching parameters to obtain maximum amount of zinc in leach liquor has been established. The leach liquor has been purified with respect to soluble impurities and the purified leach liquor has been electrolysed to obtain zinc. The different steps involved in this work are described below:

1) Sample was collected in lump form, made into small parts by drilling and ball milling and freed of solid particles of metallic zinc.
2) The ash was freed of chlorine and the conditions of removal of chlorine have been established.

3) The fine ash has been treated with sulfuric acid to get zinc sulfate solution. Different leaching parameters: particle size, acid concentration, solid/liquid ratio, time and temperature of leaching have been investigated to determine the optimum leaching conditions.
4) The leach solution has been purified with respect to the soluble impurities. The conditions of removal of the impurities have been determined.
5) The purified solution has been electrolysed in an electrolytic cell to get electrolytic zinc.

CHAPTER 3
EXPERIMENTAL

3.1 Introduction

Zinc is very useful as a protective coating for steel because in most environments to which steel is subjected, zinc acts as the anode; i.e. it dissolves in preference to the steel. In simplistic terms, while there is zinc on the surface, the steel is protected from corrosion. Hot dip galvanizing is one of a number of methods available to the surface finisher for applying a zinc coating to an item. In hot dip galvanizing, a uniform coating of metallurgically bonded zinc-iron layer is produced [1].

Zinc ash is manually skimmed from top of galvanizing bath and discarded. The ash consists mostly of oxidized zinc that forms on the surface of molten zinc metal in galvanizing pot along with some impurities included from galvanizing operation. The aim of this work is to recycle the zinc from this discarded ash.

Zinc ash was collected from a local galvanizing plant in lump form. The lump was then made into fine particles by drilling and subsequent ball milling. Chemical analysis by XRF revealed the presence of chlorine in the ash sample. Chlorine is detrimental for subsequent electrolysis. For chlorine removal two techniques were applied: calcinations [2,3] and washing with distilled water [6]. Washing with distilled water resulted effective chlorine removal. After washing with distilled water chlorine free ash sample was filtered, dried and again make into fine powder by ball milling and then sieved into different sizes. Particles of different sizes were subjected to leaching with diluted sulfuric acid under different process parameters and the optimum conditions for leaching were established to maximize the amount of zinc in leach liquor. The activation energy was also determined by both integral and differential approach.

After leaching, the leach liquor was separated from unwanted residue by filtration. In leach liquor, along with zinc, other impurities also go into solution and these impurities are detrimental for subsequent electrolysis. So, these impurities were removed by applying pH controlled precipitation and cementation. By finishing purification, the leach liquor was electrolysed for getting pure zinc successfully.

For electrowinning, leach liquor composition (concentration of Zn and concentration of H_2SO_4) was varied to get maximum current efficiency. Current densities were also varied to get the effective current density for getting high current efficiency. After getting effective current density and desirable bath composition, a long term experiment was carried out to determine the minimum concentration of zinc in electrolytic solution where electrowinning should be stopped to keep current efficiency within acceptable region. From this long term experiment, it was also evident that the concentration of H_2SO_4 increased gradually in the solution with continued zinc deposition and that free sulphuric acid could be recycled to leach more ash sample. These are overall brief experimental procedures followed in this work and are described below in details sequentially.

3.2 Drilling and Ball Milling

The discarded zinc ash from a galvanizing plant was collected and at first it is made into small parts by using a drill machine and then ground in a ball mill for several hours to get fine particles of zinc ash.

3.3 Compositional Analysis

The powders of ash were analyzed by X-Ray Fluorescence (XRF). The sample analyzed in X-Ray Fluorescence machine was prepared in the following way.

a) About 2 gm of samples was finely ground in an agate mortar. The powder was made moisture free.
b) The powder was then pressed in a hand press machine to make disk shaped sample.
c) The disk shaped samples were placed in the machine for analysis.

3.4 Chlorine Removal

Two methods were followed for chlorine removal: calcinations [2, 3] and washing with distilled water [6].

3.4.1 Calcination

Calcination was carried out at five different temperatures of 500^{o}C, 600^{o}C, 700^{o}C, 800^{o}C and 900^{o}C. The duration of calcination was taken as 2 hours for every temperature. Five grams of ash sample was taken in a silica crucible and was put inside the electrically heated muffle furnace of Gallenkamp brand for the required time. The weight of sample was measured after 10, 20, 30, 60, 90 and 120 minutes.

3.4.2 Washing with Distilled Water

Washing with distilled water was carried out to remove chlorine present in the ash. The parameters studied for effective chlorine removal were: liquid/solid ratio, washing temperature and washing time [6].

3.4.2.1 Liquid/solid Ratio Optimization

500 ml distilled water was taken in a beaker of 1000 ml capacity and the required amount of sample was added to maintain the required liquid/solid ratio. Washing temperature was maintained constant at 80°C. After every 5 minutes, 2 ml solution was taken and tested for detecting chlorine in solution by adding freshly prepared solution of 0.1N $AgNO_3$. If chlorine is present, then white precipitate of silver chloride is formed [51]. The experiment was continued for as long as chlorine is detected in the used distilled water. Thus optimum liquid/solid ratio was determined.

3.4.2.1 Washing Temperature Optimization

After getting optimum liquid/solid ratio, attempts were made to determine optimum washing temperature. Washing temperatures of 60°C, 70°C, 80°C and 90°C were studied. After every 5 minutes, 2 ml solution was taken and was tested for detecting chlorine in solution by the addition of freshly prepared solution of 0.1N $AgNO_3$. Presence of chlorine in the used distilled water was identified by the appearance of white precipitate with the addition of silver nitrate. The experiment was continued as long as chlorine was detected in the used distilled water. After finishing the experiment, the used distilled water was separated by filtration and analyzed for zinc determination, as it was suspected that there may be some loss of zinc as zinc chloride.

3.5 Ball Milling and Sieving

After chlorine removal by washing with distilled water, the ash particles became agglomerated. The agglomerated sample was then dried and subjected to ball milling to break agglomeration into fine particles. After ball milling, different size fraction of powder was separated by using a standard sieve shaker. The sieves of different mesh sizes were arranged in such a way that the sieves were placed from top to bottom according to their increasing sieve no. 200 gm of ground ash was then placed in the top most sieve and the powder was shaked for 15 minutes. Then the samples retained on different sieves were collected for further leaching. Five size fractions were taken for study. These were -40+70 mesh, -70 + 100 mesh, - 100 + 140 mesh, - 140 + 200 mesh, - 200 + 270 mesh.

3.6 Leaching

Different sized ash particles were leached in a round bottom flask assembled with reflux condenser. The round bottom flask was heated by a mantle heater. Leaching experimental set up is shown in Figure 3.1. Leaching reagent sulfuric acid of different concentrations was prepared in a 500 ml volumetric flask. Due to exothermic nature of leaching reaction, a water bath and ice (when needed) was used for maintaining required temperature. Sulfuric acid of different concentrations was used for dissolution of zinc. During acid dilution, heat was evolved and, therefore, diluted acid was cooled before adding zinc ash into it.

For all of the leaching experiments, 60 gm of solids (ash) was leached in liquid H_2SO_4. For AAS analysis, 1 ml leach liquor was taken with a 3 ml syringe. The investigated leaching parameters [4] are summarized in Table 3.1.

3.6.1 Effect of Powder Size

The powder samples were leached with 3.2 M H_2SO_4 with a solid/liquid ratio of 1:5 gm/ml at 50°C temperature for 100 minutes. Leaching of -40+70 mesh, -70+100 mesh, -100+140 mesh, -140+200 mesh and -200+270 mesh powder size was studied. Extraction of zinc i.e. concentration of zinc in the solution was plotted against mesh size. The mesh size that gave the maximum level of extraction was decided from these plots.

3.6.2 Effect of Concentration of Leaching Reagent

The powder size that showed maximum extraction was then leached with sulfuric acid of different concentrations to determine the effect of leaching reagent concentration at 50°C with a solid-liquid ratio of 1:5 gm/ml and a time period of 100 minutes. The studied concentrations of sulfuric acid were 1.8M, 2.7M, 3.2M, 3.6M and 4.4M. Zinc concentration in the solution i.e. the extraction of zinc from the source material at different time was plotted against time. The optimum concentration of sulfuric acid regarding extraction was decided from those plots.

3.6.3 Effect of Liquid/solid Ratio

The leaching was conducted at different leach liquor volume of same acid concentration (3.2 M H_2SO_4) against 60 gm solid sample for 100 minutes at 50°C. For 60 gm of sample 120ml, 240ml, 300ml, 360ml, 420ml volume of leaching solution was chosen. Zinc concentration in the leach liquor at different liquid/solid ratio was plotted and the optimum liquid/solid ratio regarding extraction was decided.

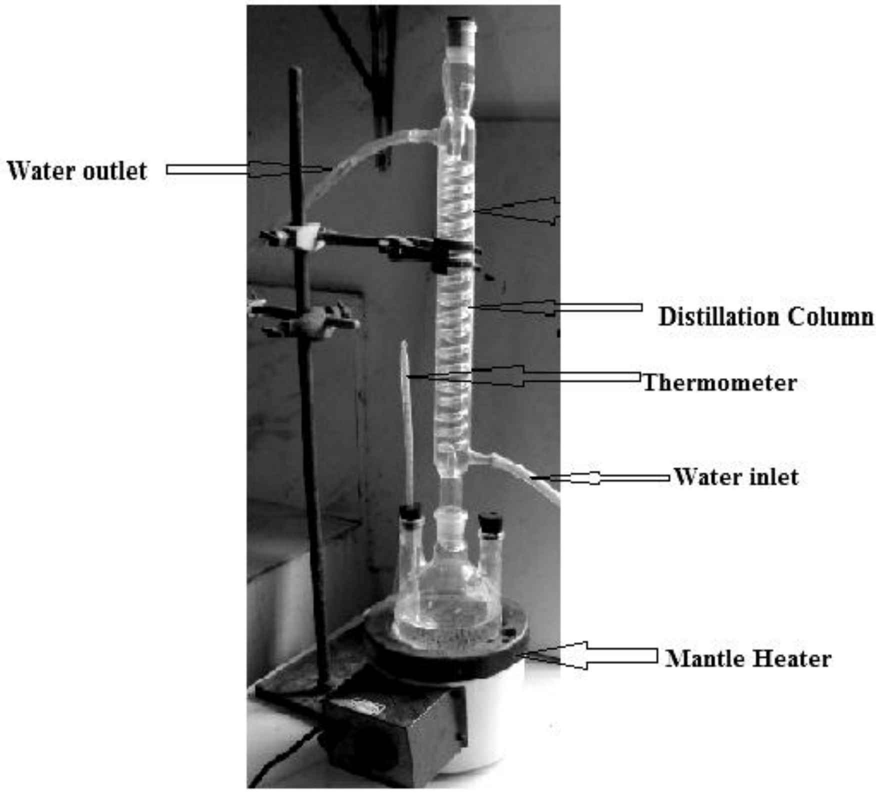


Fig. 3.1: The leaching set-up.

Table 3.1: List of the investigated leaching parameters.

Name of parameters studied	Values of parameters studied	Other constant parameters
Powder size	-40+70 mesh	50^{o}C, concentration of H_2SO_4 of 3.2M, solid liquid ratio of 1:5 gm/ml
	-70+100 mesh	
	-100+140 mesh	
	-140+200 mesh	
	-200+270 mesh	
Concentration of leaching reagent (sulfuric acid)	1.8 M	50^{o}C, powder size that gives better extraction, solid liquid ratio of 1:5 gm/ml
	2.7 M	
	3.2 M	
	3.6 M	
	4.4 M	
Liquid/solid ratio	2	50^{o}C, powder size that gives better extraction, concentration of H_2SO_4 that gives better extraction
	4	
	5	
	6	
	7	
Time	20	Parameters (powder size, concentration of H_2SO_4, liquid/solid ratio) that give better extraction at 50^{o}C
	40	
	60	
	80	
	100	
	140	
	180	
	240	
Temperature	40^{o}C	Powder size that gives better extraction, concentration of H_2SO_4 that gives better extraction, optimum liquid/solid ratio
	50^{o}C	
	60^{o}C	
	70^{o}C	

3.6.4 Effect of Time

The particle size that gave the maximum extraction was leached with sulfuric acid of optimum concentration with the optimum liquid/solid ratio of 5:1 ml/gm at temperature of 50^{o}C for 20 minutes, 40 minutes, 60 minutes, 80 minutes, 100 minutes, 140 minutes, 180 minutes, and 240 minutes. The results were plotted to get optimum time for leaching.

3.6.5 Effect of Temperature

Ash particles were leached with all the established optimum parameters at four different temperatures of 40^{o}C, 50^{o}C, 60^{o}C, and 70^{o}C. Zinc concentration in the solution i.e. the extraction of zinc from the source material at different time was plotted against time. From those plots the optimum temperature that gave the maximum extraction during leaching was established. Activation energy was determined by both the integral and differential approach.

3.6.6 Analysis of Leach Liquor

For all leaching experiments, 1 ml leach liquor was collected by 3 ml syringe and was taken in plastic bottles for analysis. The samples were analyzed for zinc using Atomic Absorption Spectrophotometer (AAS) of Varian AA240FS model. The AAS machine was calibrated with 0.1mg/L, 0.2mg/L, 0.5mg/L, 1.0mg/L and 1.5 mg/L of standard Zn solution. The AAS machine used has the zinc measuring range of 0.50 mg/L to 1.2 mg/L. So, the samples were diluted at different dilution to get the results within that range and the final results were obtained after multiplying the machine results with the dilution factor.

3.7 Purification of the Leaching Solution

3.7.1 P^H Controlled Precipitation

Purification was conducted for iron removal by air blowing in presence of MnO_2. At this stage,

1.0 g/l of manganese dioxide was added to the solution and the pH was adjusted at 4.5 – 5.2 using calcium hydroxide. Air was passed through the solution for 2h, where the color was changed to brown yellow, during which the temperature was maintained between 70-80^oC. After every 2 hours, the solution was filtered and the precipitated iron was removed [8]. The filtrate was then tested for iron detection by the addition of potassium ferrocyanide. Appearance of bluish color with addition of potassium ferrocyanide indicated the presence of iron [51]. As long as iron was detected, the purification was repeated and the repetition was continued for five times. Every time, purification was carried out for two hours. After the removal of iron, the filtrate containing concentrated zinc sulphate along with minor impurities was sent for further three stages of purification.

3.7.2 Cementation

First stage purification was carried out by the addition of zinc dust at ambient temperature.

Second stage purification is done by cementation with zinc dust at higher temperatures of about 85^oC (hot purification) in the presence of potassium antimony tartarate.

In the third and final purification step, activated charcoal was added to the purified solution to adsorb unwanted organics and impurities.

After these three stages of purification, the leach liquor was tested qualitatively by the addition of dilute HCl, acid solution of H_2S, basic solution of H_2S and sodium carbonate sequentially. If any precipitate formed with that sequential addition of reagent, then those three stages of cementation technique was repeated.

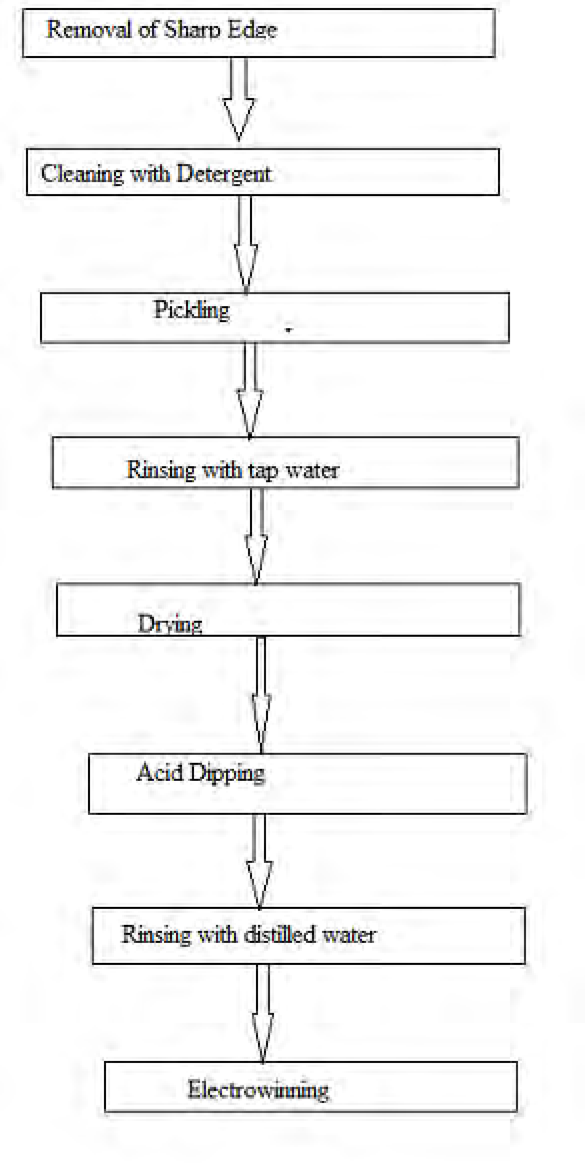
3.8 Zinc Electrowinning

3.8.1 Materials:

Commercial aluminum sheets were used as substrates for zinc deposition in this investigation. As anodes for electrodeposition lead sheets were used. The size of lead anode was 35 mm×15 mm×0.4 mm and that of aluminum substrate was 50 mm×15 mm×1 mm.

3.8.2 Preparation of Aluminum Cathode for Electrowinning

The flow diagram of sample preparation is as follows:



3.8.2.1 Removal of Sharp Edges

Sharp edges were removed by grinding. Current density becomes larger at sharp edges. To maintain uniform current density, sharp edges were removed.

3.8.2.2 Cleaning with Detergent

The sample might contain grease, oil, drawing compounds and other substances which came during its fabrication. Presence of those contaminants would weaken the subsequent pickling action on the sample. So those were removed by using a solution of commercial Na_2CO_3 powder.

3.8.2.3 Pickling

Pickling was done for the chemical removal of surface oxides (scale) and other contaminants such as dirt from metal by immersion in an aqueous acid solution. Particulars of pickling operation are given in Table 3.2.

3.8.2.4 Rinsing

Thorough rinsing was done for obtaining the clean, stain-free and smut-free surface necessary for the subsequent operation. In order to get optimum rinsing conditions, maintenance of the high pressure cold water sprays were provided. Thus, acid contamination was eliminated or minimized.

3.8.2.5 Acid Dipping

Samples were acid dipped to neutralize any residual film, remove oxides and smuts to activate the work piece for subsequent electrowinning. Various parameters of this treatment are given in Table 3.2. The sample was then ready for electrowinning.

Table 3.2: Parameters of pickling and acid dipping

Name of operation	Reagents used (wt%)	Operating conditions	
		Temperature (°C)	Time
Pickling	HCl : 20 H_2O : 80	70	10 minutes
Acid dipping	HCl : 10 H_2O: 90	Room	15 seconds

3.8.3 Electrowinning Set-up

Electrowinning was carried out in a laboratory type electrodeposition set-up consisting of a beaker, a D.C. power supply, a thermometer and a holder. The beaker containing the leach solution was placed on a hot plate. Anode and cathode were connected to the d.c. power supply via a multimeter.

3.8.4 Electrowinning Operation

The beaker was filled to approximately two thirds of its marking point with the purified leach solution. Electrowinning was carried out in a laboratory electrolyser without electrolyte circulation under the listed in Table 3.3, chosen according to the literature [39].

Table 3.3: Electrolysis set up

Electrolyte volume:	approximately 1L
Anode:	Lead
Cathode:	Aluminium
Current density:	30, 45 and 60 mA/cm^2
Electrode distance:	20 mm
Electrolyte temperature:	30^{o}C

As cathode and anode aluminum sheet and lead sheet were used respectively. 6 Amp current was supplied at a terminal voltage 5V for the required time. To maintain required current density of 30, 45 and 60 mA/cm^2, cathode electrode area was adjusted. Zinc content and free sulfuric acid of the purified leach solution were adjusted to vary the electrolytic bath composition. Experimental conditions are listed in Table 3.4. Weight of the cathode was recorded before and after every electrolysis experiment. Current efficiency was calculated and bath composition and current density was determined for getting better current efficiency.

Table 3.4: Electrowinning parameters.

Current density A/m^2	Bath composition	
	g/L Zn	g/L H_2SO_4
30	160	40
45	160	40
60	160	40
30	120	50
45	120	50
60	120	50
30	65	90
45	65	90
60	65	90
30	50	150
45	50	150
60	50	150
30	40	80
45	40	80
60	40	80
30	40	270
45	40	270
60	40	270

A long term experiment was carried out with the optimum bath composition and optimum current density obtained from the previous experiment to obtain the variation of zinc sulfuric acid concentration and to determine the minimum concentration of zinc concentration in leach solution where electrolysis should be stopped to minimize loss of current efficiency. The long term experimental conditions are listed in Table 3.5.

Table 3.5: Parameters for long term electrowinning experiment.

Current density	Period, Hour		Bath composition	
			Zn (g/L)	H_2SO_4 (g/L)
45	3	start	120	50
45	4	End of experiment	99.2	98.4
45	4	End of experiment	69.2	140.4
45	3	End of experiment	41.2	181.6

After electrowinning an adherent deposit of zinc was obtained, which was stored for melting.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The composition of the supplied ash sample was determined by XRF analysis and the presence of chlorine was identified. Attempts were therefore made for chlorine removal by applying two techniques: calcination and washing with distilled water. Between two techniques, the second technique „washing with distilled water" was found to be effective for chlorine removal. The chlorine free ash sample was separated from the distilled water used for washing by filtration. Then the sample was dried, ball milled and sieved into different size fractions by using sieve shaker. The different sized particles were subjected to leaching. The particle size corresponding to the best extraction was used for further study of getting optimum leaching reagent (H_2SO_4) concentration, optimum liquid/solid ratio, optimum time and optimum temperature for getting optimum amount of zinc in leach liquor. The activation energy was also calculated. The problem associated with leaching is that not only zinc goes into solution, but also other impurities (detected by XRF analysis) go into solution. In the hydrometallurgical route of zinc recovery, electrolysis would be the final step to get pure zinc from ash and the presence of impurities would create serious problems in electrowinnig. So, removal of impurities was one of the important steps. Iron and aluminium were removed by pH controlled precipitation. Other impurities were removed by cementation. Electrowinning of zinc was carried out from the purified leach liquor. During electrowinning, the effect of bath composition (concentration of zinc and free sulfuric acid) and current density on current efficiency was investigated. The minimum concentration of zinc in electrolytic bath where electrowinning should be stopped was established. The variation of concentration of free sulfuric acid in the electrolytic leach liquor with time was also recorded. The results of all these investigations are described below sequentially.

4.2 Compositional Analysis

The composition obtained through XRF analysis is given in Table 4.1.

Table 4.1: Typical composition (%wt) of nonpurified ash (as received composition).

Zn	Fe	Pb	Cu	Sn	Al	Cl	Si	Mn	Mg	Ni	Cd,Cr
62	11	17	1.02	2.2	4.6	1.4	0.3	0.10	0.20	0.15	<0.03

In XRF analysis, it was found that about 62% zinc was present in the ash with some other unwanted impurities. The impurities would cause serious problems during electrolysis. Calcinations and washing methods were tried to remove chlorine. Precipitation and cementation techniques were carried out to remove iron and other impurities.

4.3 Chlorine Removal

Chlorine would have several detrimental effects [16]. Chlorine would form perchloric acid at anode, cause severe corrosion to anode, thus produce lead ions from lead anode used during electrolysis. Lead ions would contaminate the cathode deposit of zinc. The most dangerous effect of chlorine would be the production of chlorine gas at anode during electrolysis which is dangerous to cell operators [16]. Two methods calcination [2,3] and washing with distilled water were attempted to remove chlorine from sample.

4.3.1 Calcination

Calcination was carried out in an electrically heated muffle furnace by heating the ash sample for different times at specified temperatures. Clacination results are summarized in Table 4.2 and are plotted in Fig. 4.1.

Table 4.2: Results of calcination.

Calcination Time (Min.)	Weight (gm) before calcination	Weight (gm) after calcinations				
		900°C	800°C	700°C	600°C	500°C
10	5	5.1	5.09	5.08	5.075	5.0845
20	5	5.12	5.1	5.09	5.085	5.126
30	5	5.14	5.13	5.129	5.127	5.173
60	5	5.2	5.18	5.175	5.174	5.2
90	5	5.23	5.21	5.205	5.2	5.22
120	5	5.25	5.24	5.235	5.23	5.0845

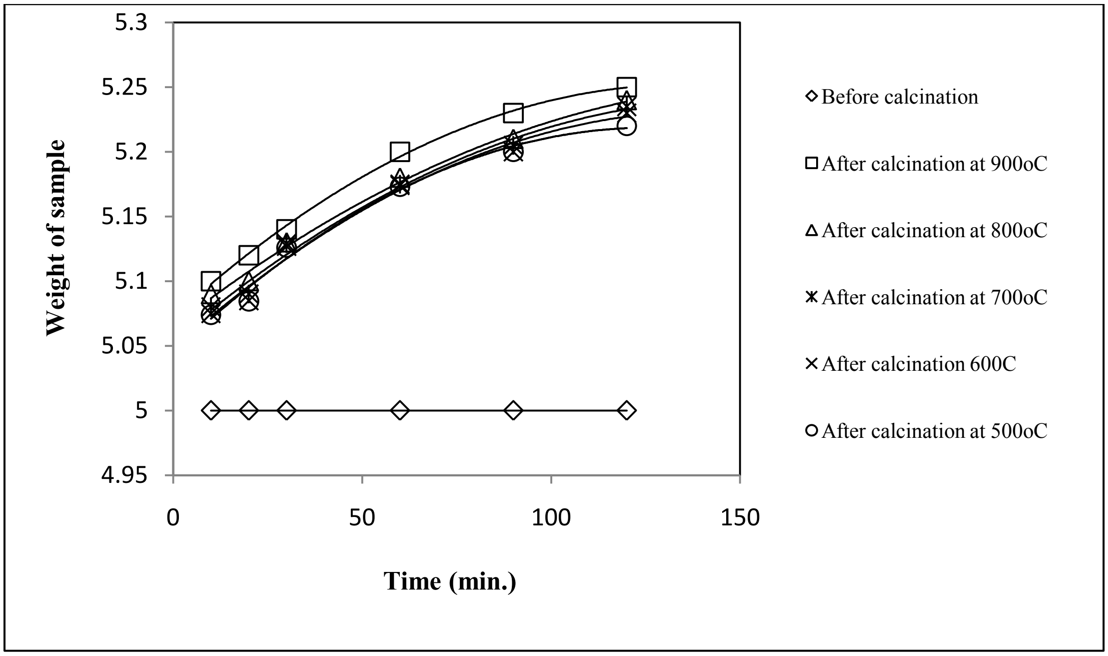


Fig. 4.1: Weight vs. time plot for calcination.

It was anticipated that if chlorine would be removed by calcination, then there should be some loss in weight of the sample after calcination. Weight loss was considered as a primary indication of chlorine removal. But it was found that instead of decrease in weight, the weight of the sample was increasing gradually with time of calcinations at every calcinations temperature. Weight gain instead of weight loss did not give any clue about chlorine removal. Weight gain might be due to oxidation of the sample during calcination. The calcined sample was then attempted to be leached in sulfuric acid. At first concentrated and then diluted sulfuric acid was used to leach the calcined ash, but it was found that the calcined ash remained inert in the leaching reagent. In fact, from calcination it was not well established whether chlorine was removed or not, the inertness of the calcined sample to leaching reagent appeared as the main problem for the hydrometallirgical route that would be followed. The problem of inertness of the calcined sample might be attributed to the formation of a complex of zinc and iron with oxygen due to high concentration of iron in the sample [3]. Due to that problem, calcination route of chlorine removal was not followed further; rather the other method of washing with distilled water was studied.

4.3.2 Washing with Distilled Water

Washing with distilled water removed chlorine present in the ash. The parameters studied for effective chlorine removal were: liquid/solid ratio, washing temperature and washing time [6]. Attempts were made to optimize these parameters. The target of optimization of those parameters was twofold: to reduce volume of required distilled water and to minimize loss of zinc in that washing medium. The presence of chlorine in the used water was identified qualitatively by adding freshly prepared 0.1N silver nitrate solution. The appearance of white precipitate of silver chloride indicated the presence of chlorine in used water. If no white colored precipitate appeared, it indicated that no further chlorine was going into water, i.e., no further chlorine was present in sample.

4.3.2.1 Liquid/solid Ratio Optimization

Liquid/solid ratios of 2, 4, 6, 8, 10, 12 and 14 were studied for washing. Washing with different liquid/solid ratios are summarized in Table 4.3 and are plotted in Fig. 4.2. From these plots, it is found that as the liquid/solid ratio increases, the required time for washing decreases. This supports the fact that as the volume of distilled water compared to solid increases, the concentration gradient of chlorine between the sample and the distilled water increases, thus chlorine goes to the liquid (distilled water) quickly. However, liquid/solid ratios of more than 10 did not result in significant decrease in the required time for chlorine removal. Liquid/solid ratio of 10 was taken as the optimum condition for washing.

Table 4.3: Liquid/solid ratio vs. time for washing with distilled water.

Liquid/solid ratio (ml/gm)	**Required time (min.)**	**Constant parameter**
2	60	Temperature of 80^{o}C
4	50	
6	40	
8	35	
10	30	
12	30	
14	30	

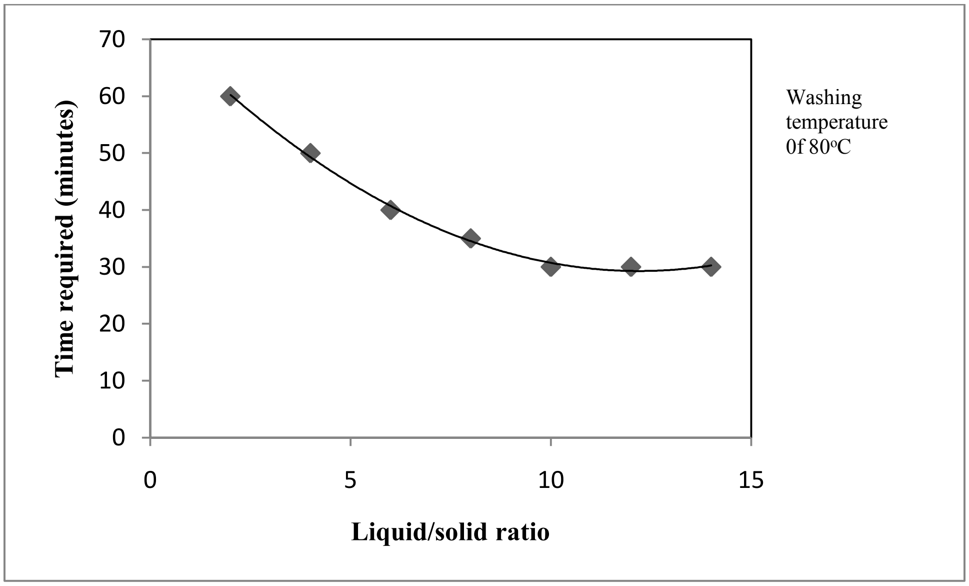


Fig. 4.2: Liquid/solid ratio optimization curve for washing.

4.3.2.2 Washing Temperature Optimization

Washing temperatures of 60°C, 70°C, 80°C and 90°C were studied for effective chlorine removal. The results of washing at different temperatures are summarized in Table 4.4 and are plotted in Fig. 4.3. It can be concluded that as washing temperature increases, the required time for chlorine removal decreases. As washing temperature increases, chlorine goes into solution rapidly. But the required time levels off at around 80°C, beyond 80°C, there is no significant decrease in time required for effective chlorine removal. So, 80°C can be taken as the optimum temperature for chlorine removal.

Table 4.4: Washing temperature vs. time for washing with distilled water.

Washing Temperature (°C)	**Required time for chlorine removal (min.)**	**Constant parameter**
60	60	Liquid/solid ratio of 10:1 (ml/gm)
70	40	
80	30	
90	29	

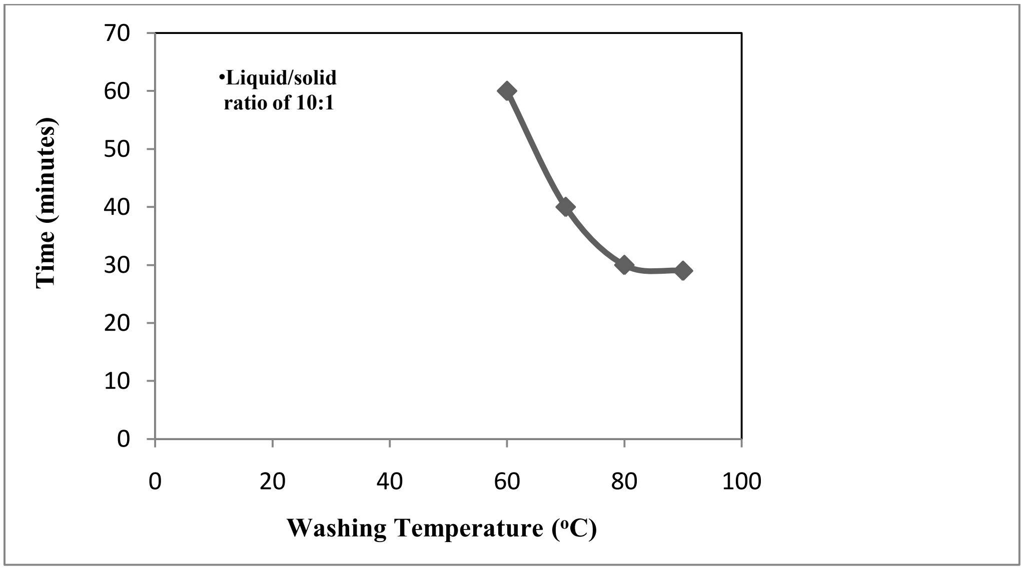


Fig. 4.3: Temperature optimization curve for washing.

From those observations, it could be concluded that washing zinc ash with distilled water for half-an hour at 80°C, removed chlorine present in the sample. After washing, the used distilled water was analyzed for zinc concentration and it was found that about 1 g/l Zn (which is about 1.5% of zinc present in the sample) was present in the used water. That minor loss of zinc can be compromised for removal of detrimental chlorine content for electrowinning.

4.4 Leaching Results

4.4.1 Particle Size Optimization

Five size fractions were taken for study. Those were -40+70 mesh, -70+100 mesh, -100+140 mesh, -140+200 mesh, and -200+270 mesh. Results of leaching with different particle sizes are summarized in Table 4.5 and are plotted in Fig. 4.4. Fig. 4.4 shows that the higher the mesh-size the more is the extraction and powder size of -200+270 mesh showed maximum extraction [51]. This is compatible with the theoretical understanding that small particles have more surface than bigger particles have and hence leaching reagent gets more surface to have contact with the sample powders.

Table 4.5: Results of leaching for different powder size of zinc ash.

Mesh size	Zinc concentration in solution (g/L)
70	50
100	60
140	65
200	75
270	80

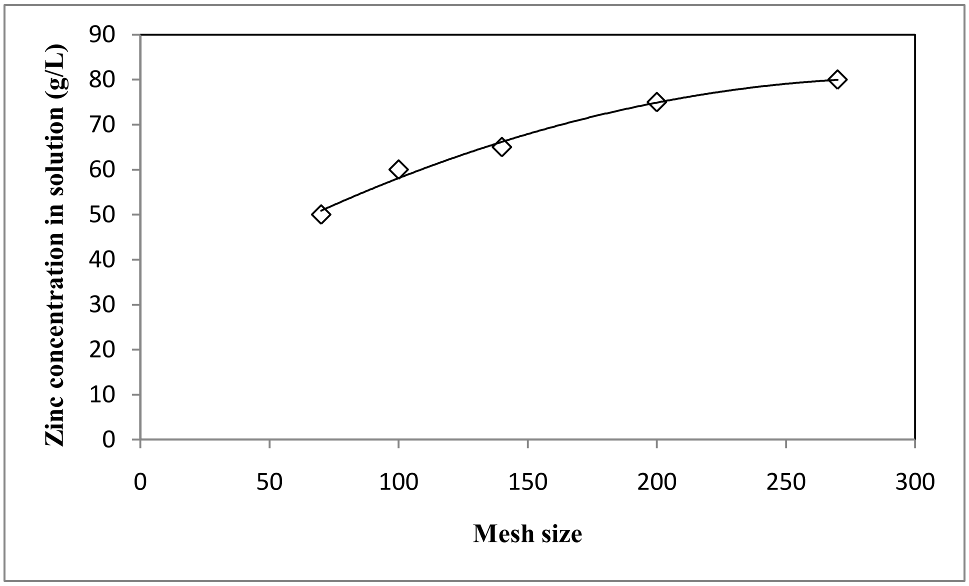


Fig. 4.4: Leaching of different powder size of the sample.

4.4.2 Concentration Optimization

Zinc ash sample of -200+270 mesh was leached with sulfuric acid of 1.8 M, 2.7 M, 3.2 M, 3.6 M and 4.4 M for 100 minutes with liquid/solid ratio of 5 maintaining constant temperature of 50°C. Results of leaching with different concentration are summarized in Table 4.6 and plotted in Fig. 4.5. From Fig.4.5, it is observed that zinc concentration in solution increases with increase in sulfuric acid concentration. The rate of zinc dissolution was higher in the initial period of dissolution. The zinc concentration in solution after 140 minutes for each acid concentration is plotted in Fig.4.6 and it is observed that zinc dissolution increases rapidly with increase in acid concentration up to concentration of 3.2 M H_2SO_4, beyond 3.2 M zinc dissolution with acid concentration did not increases so steeply. 3.2 M H_2SO_4 was considered as optimum acid concentration for effective leaching.

Table 4.6: Results of leaching for different concentration of leaching reagent (H_2SO_4).

Time (Minutes)	Zinc Concentration in solution (g/L)				
	1.8 M H_2SO_4	2.7 M H_2SO_4	3.2 M H_2SO_4	3.6 M H_2SO_4	4.4 M H_2SO_4
0	0	0	0	0	0
20	10	25	30	33	37
40	18	30	50	52	56
60	27	50	61	64	70
80	35	60	72	75	79
100	40	65	80	85	90
140	45	70	81	86	91

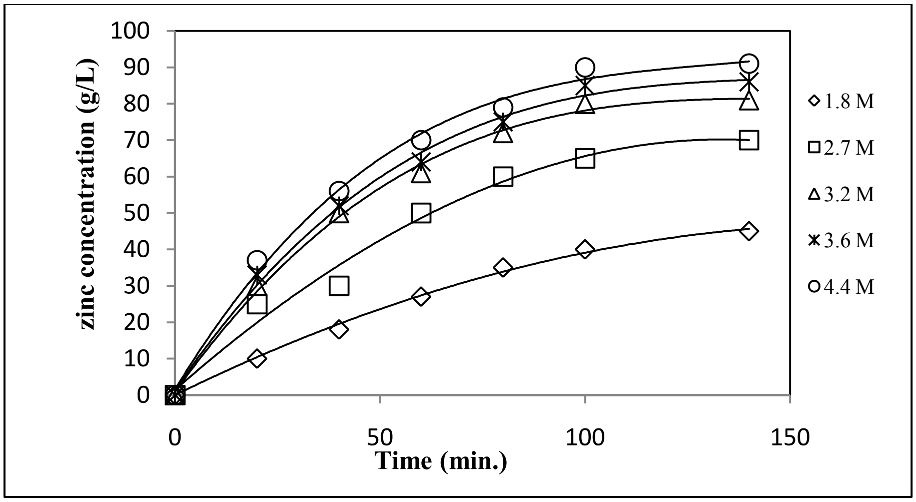


Fig. 4.5: Leaching with time for different leaching reagent concentration.

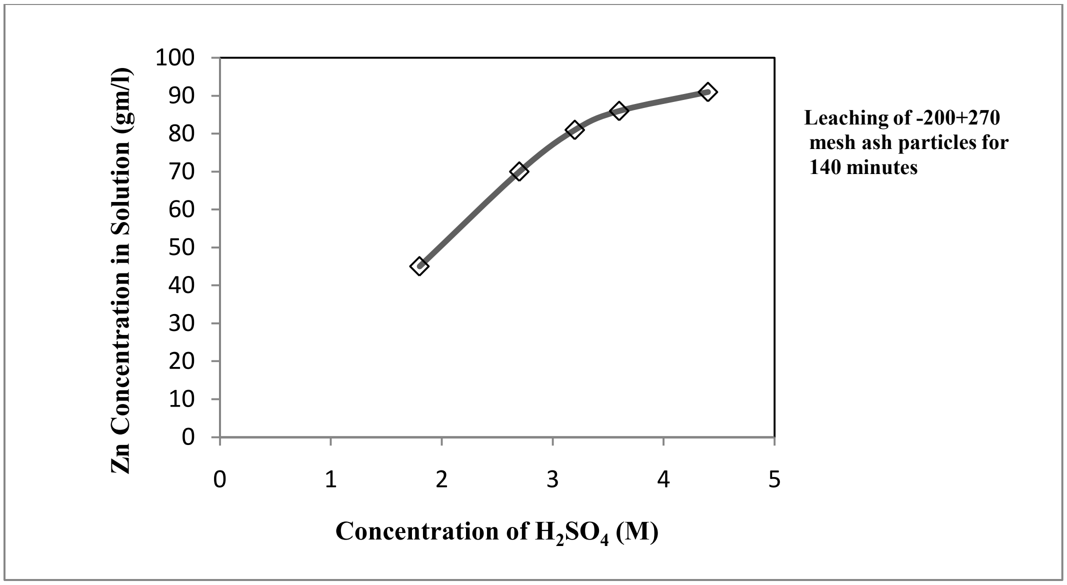


Fig. 4.6: Leaching for 140 minutes for different leaching reagent concentration.

4.4.3 Liquid/solid Ratio Optimization

Ash sample of -200+270 mesh was leached with 3.2 M H_2SO_4 for 100 min with different liquid/solid ratio of 2, 4, 5, 6 and 7 at 50^oC. Results are summarized in Table 4.7 and are plotted in Fig. 4.7. Concentration of zinc in solution increases significantly with increase in liquid/solid ratio up to liquid/solid ratio of 5, beyond liquid/solid ratio of 5, there is no significant increase in zinc concentration with increasing liquid/solid ratio. Liquid/solid ratio of 5 was taken as the optimum condition for effective leaching.

Table 4.7: Results of leaching for different liquid/solid ratio of leaching reagent (H_2SO_4).

Liquid/solid Ratio	Zinc conc. in solution (g/L)
2	40
4	70
5	80
6	82
7	83

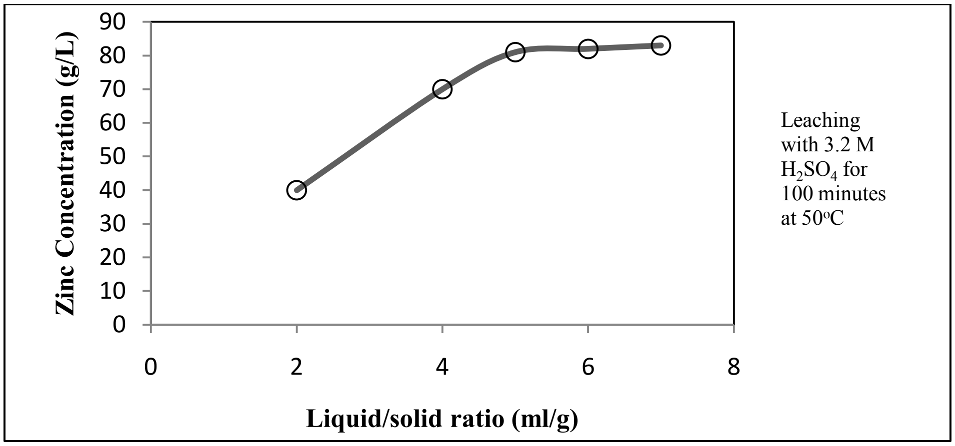


Fig. 4.7: Leaching with time for different liquid/solid ratio.

4.4.4 Time Optimization

All the optimum condition obtained above was applied during leaching to determine the optimum time of leaching after which leaching rate falls to extent that no further considerable extraction occurs. The leaching was carried out with -200+270 mesh, 3.2 M H_2SO_4, solid-liquid ratio of 1:5 at 50°C up to 4 hour. Results are summarized in Table 4.8 and are plotted in Fig. 4.8. From Fig.4.8 it is evident after 140 minutes the extraction curve with time becomes almost horizontal i.e. no further considerable extraction occurs.

Table 4.8: Extent of reaction with time.

Time (min.)	Zn concentration in solution (g/L)
0	0
20	27
40	40
60	60
80	70
100	80
140	85
180	86.5
240	87

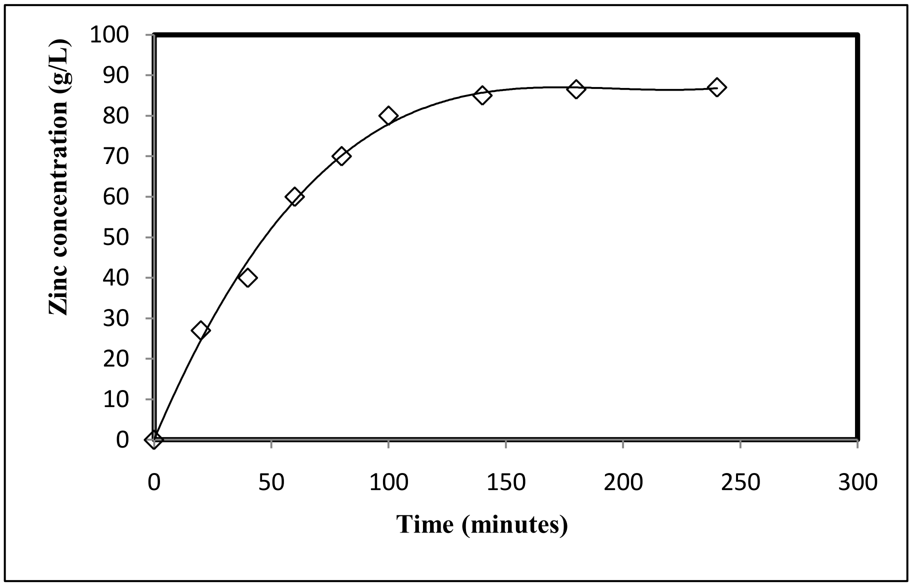


Fig. 4.8: Leaching of zinc with time with a set of variables that gave better extraction.

4.4.5 Temperature Optimization

The sample was leached with 3.2 M H_2SO_4 for 140 minutes with liquid/solid ratio of 5 at four different temperatures. Effect of temperature was studied by varying the temperature of 40°C, 50°C, 60°C and 70°C. Zinc concentrations in solution i.e. extent of reaction for different reaction temperature were listed in Table 4.9 and plotted in Fig. 4.9. Clearly, as reaction temperature increases, extraction also increases. The temperature was increased up to 70°C. At 70°C about 94% zinc goes into solution. That amount of zinc in solution was considered as satisfactory. Beyond 70°C vaporization of leaching medium became prominent. For those reasons, 70°C temperature was considered as the optimum temperature for leaching. At every temperature, the reaction rate was very fast in the initial period, it then decreased gradually.

Table 4.9: Leaching results for different temperatures.

Time (Minutes)	Zinc concentration in solution (g/L)			
	40°C	50°C	60°C	70°C
0	0	0	0	0
20	20	27	39	44
40	30	40	58	70
60	38	60	80	90
80	46.4	70	90	100
100	52.2	80	100	115
140	53	85	105	117

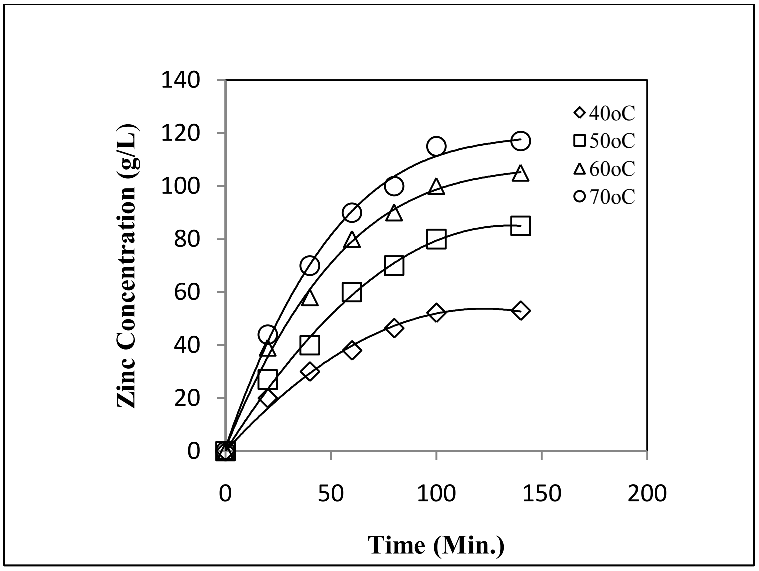


Fig. 4.9: Leaching with time at different temperatures.

4.4.6 Activation Energy Determination

4.4.6.1 Differential Approach

Activation energy was determined in three different extraction levels i.e. 50 g/L, 80 g/L and 100 g/L zinc in solution by differential approach. Reaction rates at different extraction levels for different temperature are listed in Table 4.9 and are plotted in Fig. 4.9. The equations shown in Fig. 4.9 gave the value of the slope. Activation energy for 50 g/L zinc in solution was 37.58 KJ/mol, for 80 g/L zinc in solution was 43.80 KJ/mol, and for 100 g/L zinc in solution was 47.29 KJ/mol. The average activation energy for this three extraction level is 42.89 KJ/mol or 10.41KCal/mol. There is an increasing trend in activation energy value with increase in concentration of leaching medium, which might indicate that as the concentration of dissolved material increases, the reaction becomes more sluggish.

Table 4.10: Reaction rates at different extraction level for different temperatures.

Temperature (^{o}C)	Reaction Rates (g/L.min)		
	50 g/L	80 g/L	100 g/L
40	1.49		
50	1.64	1.47	
60	1.822	1.62	1.45
70	2.01	1.79	1.60

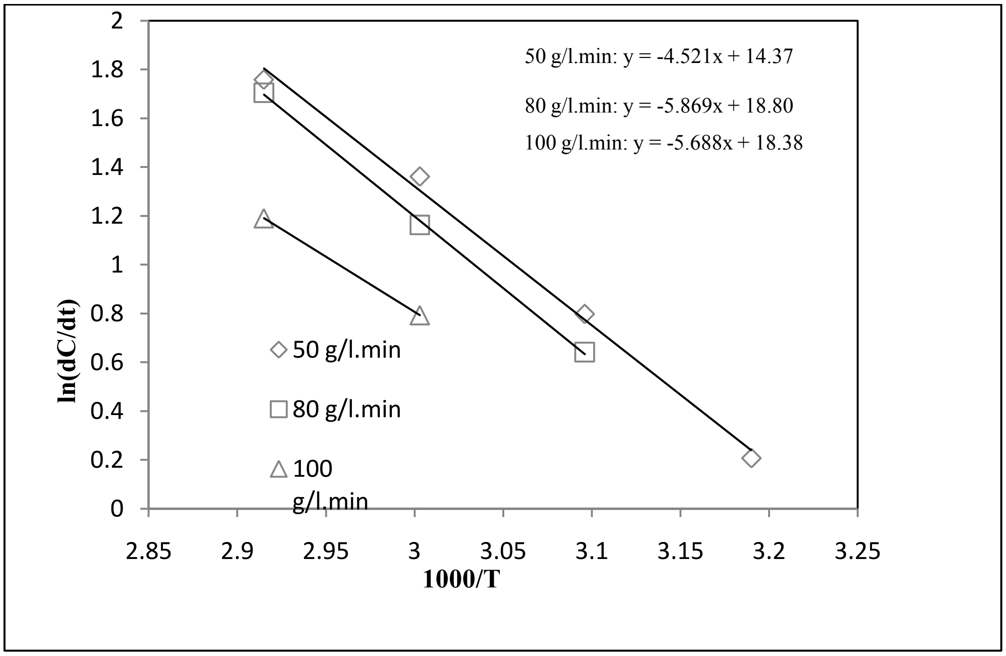


Fig. 4.10: Plots of $\ln(dC/dt)_C$ versus 1/T to determine activation energy (differential approach)

4.4.6.2 Integral Approach

The following rate equations were tried to fit to study the reaction mechanism. For the kinetics controlled by chemical reaction, the equation below would apply:

$1-(1-\alpha)^{1/3}= kt$……………….(1),

Where α=fraction reacted, t=time and k=rate constant.

Alternatively, if the kinetics were limited by diffusion through the product layer, then the following rate equations would apply:

$1-2/3\alpha-(1-\alpha)^{2/3}=kt$……………(2)

Attempts were made to fit equation 1(Fig. 4.12) and equation 2 (Fig. 4.11). It was found that data did not match equation 2. So, it can be concluded that the leaching reaction is not diffusion-controlled. The data fitted the first equation and it can be said that the leaching reaction is chemical reaction controlled.

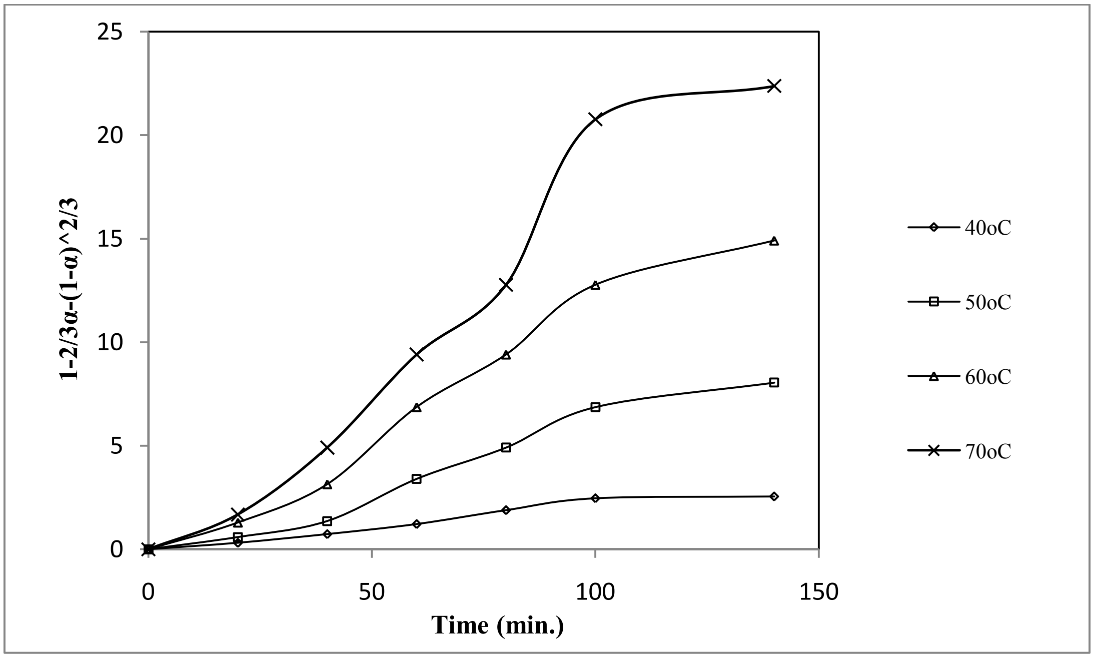


Fig. 4.11: $1-2/3\alpha-(1-\alpha)^{2/}$ vs. time plot.

The slope of each of the lines in Figure 4.12 is k which is the rate constant, and plots of k versus 1/T (Arrhenius relationship), are shown in Figure 4.13. The apparent activation energy calculated from this plot is 41.44 kJ/mol, which is very close to the activation energy value calculated by differential approach (42.89kJ/mol)

Transport – controlled reactions have been found to have activation energies in ranging from 8 to 25kJ/mol, whereas, that of chemical process is considerably higher [13]. Therefore, the apparent activation energies obtained are further evident of chemically controlled process.

Yoshida, Takashi [14] studied the activation energy determination for zinc oxide leaching by sulfuric acid and it was found that activation energy was 17.5 kJ/mol. In that experimental set-up stirring was included. But in this work, leaching experiments were carried out without any stirring. It is suggested that fine particles are formed as a result of stirring-induced spalling or abrasion [15]. These very fine particles have an increased ratio of reactive surface area to specific surface area, which results in enhancement of dissolution rate and influence activation energy [15]. The activation energy of stirred dissolution is less than the activation energy of non-stirred dissolution [15].

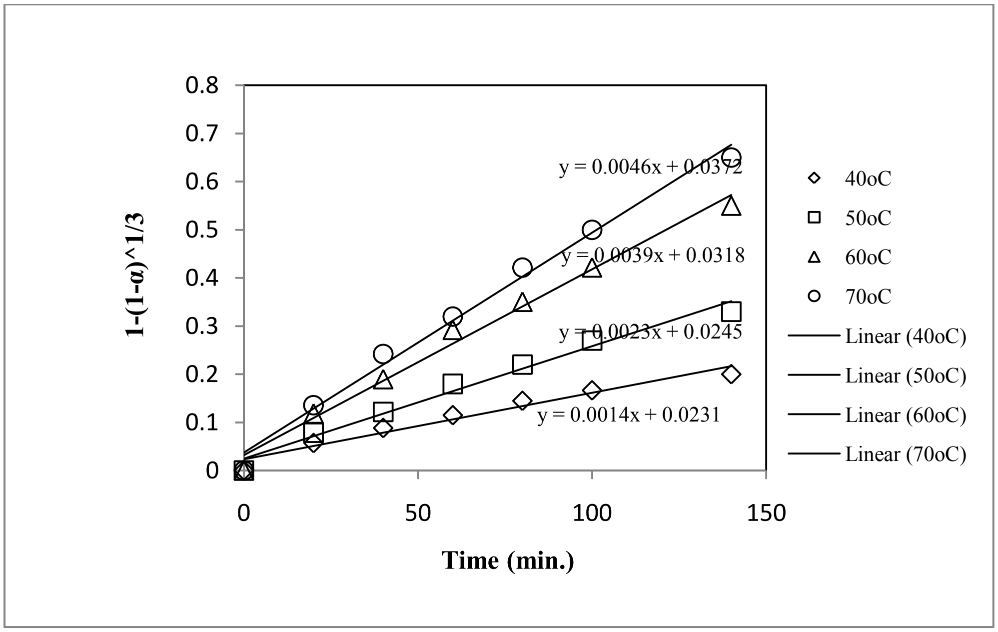


Fig. 4.12: 1-(1-α)$^{1/3}$ vs. time plot.

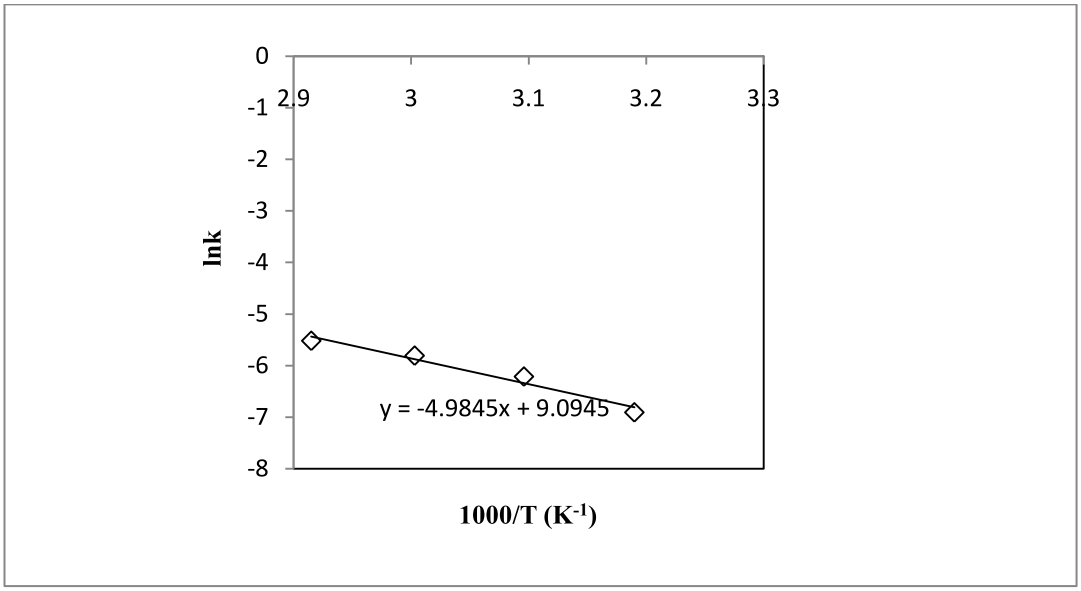


Fig. 4.13: plot of lnk vs. 1/T.

4.5 Purification

The purpose of purification was to remove impurity elements dissolved in leach liquor. Principal impurity elements detected by XRF analysis were Fe, Pb, Cu, Sn, Al, Si, Mn, Mg, Ni, Cd and Cr.

4.5.1 pH Controlled Precipitation

Iron adversely affects current efficiency of electrowinning process. At cathode reduction of ferrous oxide to ferric oxide occurs and at anode oxidation of ferric oxide to ferrous oxide occurs. The oxidation and reduction of iron circulating in the electrolyte consumes an additional amount of current. At first purification was conducted for iron removal by air blowing in presence of MnO_2. Iron is released into the solution mostly as Fe^{2+} during leaching. It was precipitated in a separate step as ferric hydroxide. Oxidation took place by sparging air into the solution. Manganese dioxide was added to assist oxidation. 1.0 g/l of manganese dioxide was added to the solution and the pH was adjusted at 4.5 – 5.2 using calcium hydroxide. Air was passed through the solution for 2h, where the color was changed to brown yellow, during which the temperature was maintained between 70-80°C. After 2 hours, the solution was filtered and the precipitated iron was removed by filtration. After the removal of iron, the filtrate liqour was tested for the presence of iron by the addition of potassium ferrocyanide. Appearance of bluish color with addition of potassium ferrocyanide indicated the presence of iron [50]. As long as iron was detected in the leach liquor, the iron purification procedure was repeated and the repetition was continued for five times in this experiment. After repeating for five times, the leach liquor did not appear as bluish color with the addition of potassium ferrocyanide, which indicated that the leach liquor was then free of iron content. After the removal of iron, the filtrate containing concentrated zinc sulfate along with minor impurities was sent for further purification consisting of three stages.

4.5.2 Cementation

The presence of nickel and cobalt produces holes in the zinc deposit at cathode. Presence of copper in electrolytic zinc sulfate solution reduces current efficiency and also contaminates zinc. Cadmium and lead has almost no effect on the current efficiency, but contaminate the cathode deposit. Presence of magnesium, manganese, silica, cadmium and aluminium has no effect on current efficiency, but contaminates the cathode deposit of zinc. Attempts were made to remove those impurities by simple cementation technique. Zinc is a highly reactive metal and this property of zinc is the basis of cementation technique. By adding powdered zinc to the solution, the zinc is oxidized and goes into solution, with the opposite side of the reaction being the reduction of the other dissolved metals back to their metallic state as follows:

$$M^{2+} + Zn = Zn^{2+} + M$$

The cementation techniques were carried out in three different stages. First stage was carried out by the addition of zinc dust at ambient temperature. This stage removed copper and cadmium as cement. The second stage was carried out at high temperatures of 85°C in the presence of potassium antimony tartarate, which removes practically all of the impurities. In the third and final step, activated charcoal was added to the purified solution to adsorb other impurities and unwanted organics (if present any). After each step the leach liquor was filtered to remove precipitated impurities. The leach liquor was then ready for electrowinning.

After these three stages of purification, the leach liquor was tested qualitatively by the addition of testing reagents according to the following sequence [Section 2.2.6.1]:

Dilute HCl is added. If lead was present then white precipitate of $PbCl_2$ is formed.

Then an acidic solution of H_2S was added. If Cu^{2+}, Cd^{2+}, Sn^{4+}, precipitate would form.

Then a basic solution of H_2S was added. If Al^{3+}, Cr^{3+}, Ni^{2+}, Mn^{2+} remained in the solution, precipitate would form.

By the addition of sodium carbonate insoluble carbonates of Mg^{2+}became precipitated.

4.6 Electrowinning

The purified solution was cooled to a temperature of 30^oC and electrolyzed in an electrolytic cell using lead anodes and aluminium cathodes maintaining a constant temperature of 30^oC. The zinc content and free sulfuric acid of the final leach solution obtained were adjusted to suit the electrolysis step. Current densities of 30, 45 and $60mA/cm^2$ were studied with different bath composition combinations of (160 g/L Zn and 40 g/L H_2SO_4), (120 g/L Zn and 50 g/L H_2SO_4), (65 g/L Zn and 90 g/L H_2SO_4), (50 g/L Zn and 150 g/L H_2SO_4), (40 g/L Zn and 80 g/L H_2SO_4) and (40 g/L Zn and 270 g/L H_2SO_4). From these different combinations of bath composition, optimum bath composition was determined to get maximum current efficiency [8, 19, 20]. After getting the optimum current efficiency, a long term experiment was carried out to determine the minimum zinc concentration in solution where electrowinning should be stopped [8].

4.6.1 Current efficiency

The change in cathode current efficiency with variable applied current densities, ranging from 30 to $60mA/cm^2$, was studied with electrolytes containing different concentrations of zinc ions and free sulfuric acid. The concentration of zinc and acid were kept constant. Experiments were performed for 3 h. The results obtained are summarized in Table 4.11.

Table 4.11: Parameters for electrowinning.

Current density A/m^2	Efficiency %	Bath composition	
		g/L Zn	g/L H_2SO_4
30	94.45	160	40
45	95.9	160	40
60	97.1	160	40
30	96	120	50
45	96.7	120	50
60	96.8	120	50
30	96.2	65	90
45	97.1	65	90
60	96.9	65	90
30	92.1	50	150
45	92.8	50	150
60	92.0	50	150
30	82.9	40	80
45	88.4	40	80
60	87.5	40	80
30	61.5	40	270
45	63.2	40	270
60	64.2	40	270

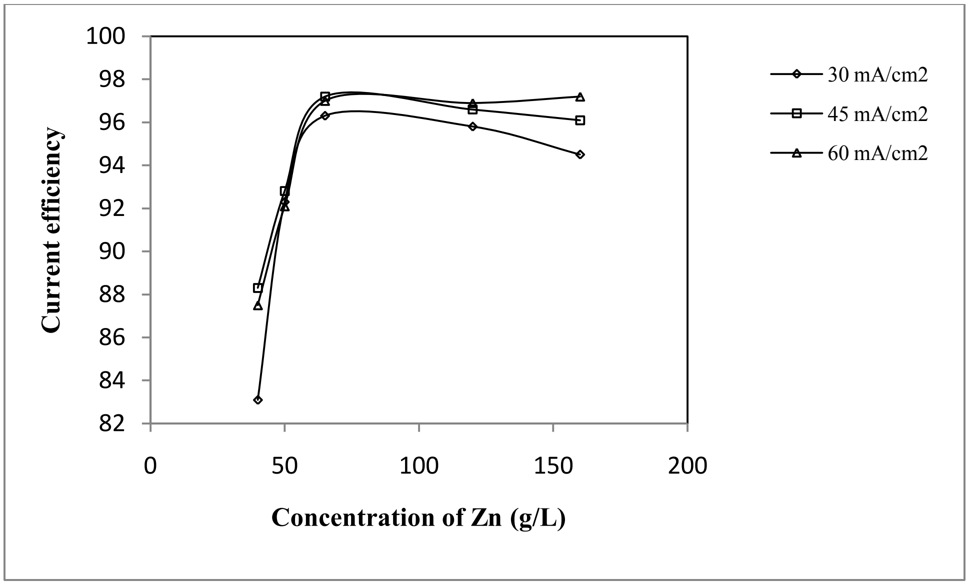


Fig. 4.13: Plot of current efficiency vs. concentration of Zn.

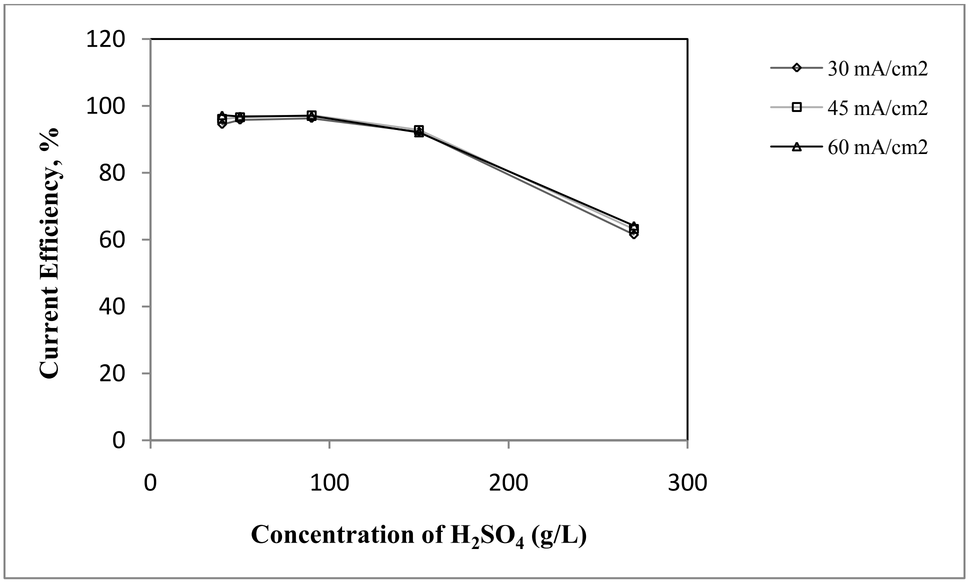


Fig. 4.14: Plot of current efficiency vs. concentration of H_2SO_4.

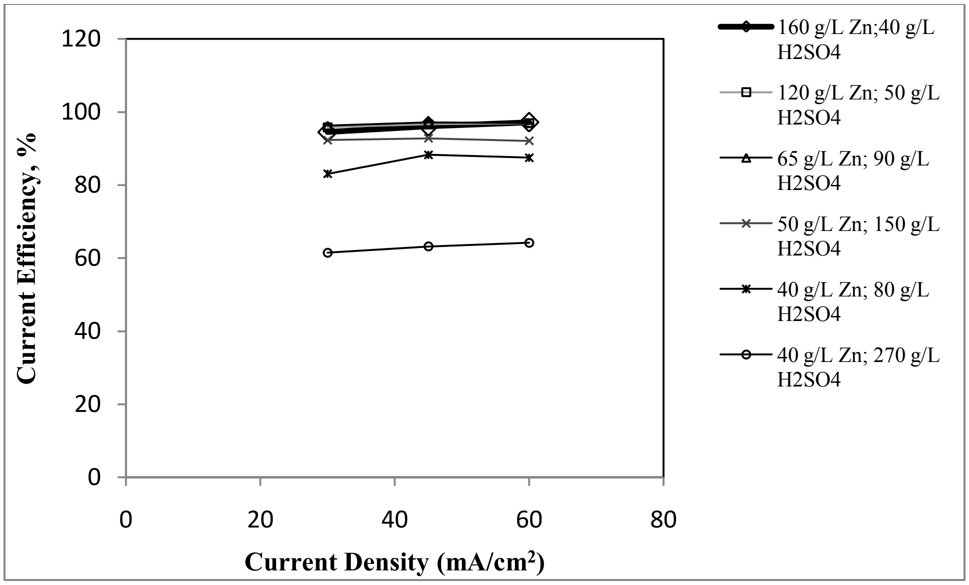


Fig. 4.15: Plot of current efficiency vs. current density.

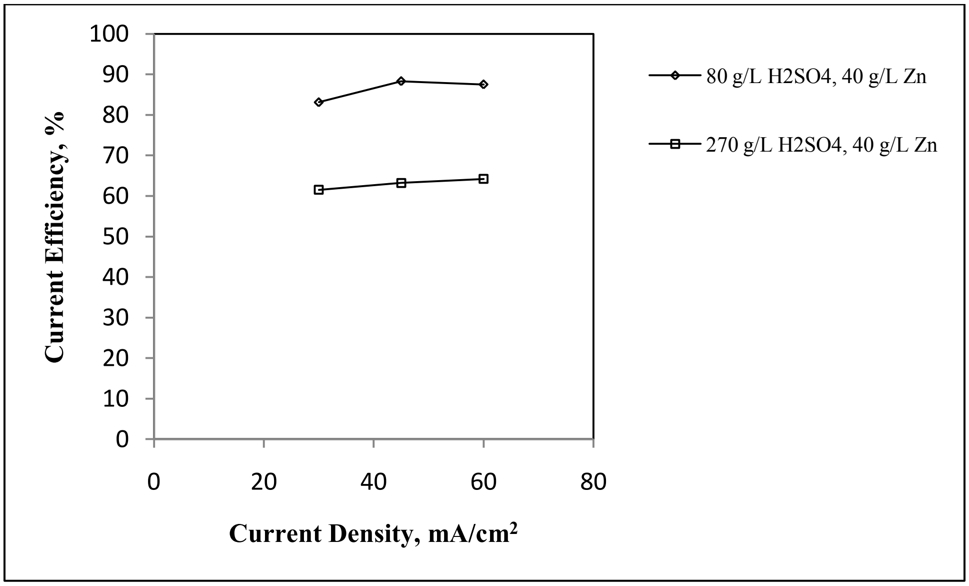


Fig. 4.16: Plot of current efficiency vs. current density.

The above results (Fig. 4.13-4.16) show that the current efficiency is high, within the current densities applied, for a wide range of concentrations for both zinc and sulfuric acid. The highly convenient results were achieved with a current density of 45mA/cm^2. The current efficiency decreased dramatically when zinc content in the electrolyte decreased to less than 40 g/L, and especially sulfuric acid increases (>80 g/L) in those experiments.

A long term experiment, using a fixed volume and one electrolyte, with a starting composition of 120 g/L and 50 g/L H_2SO_4, was performed to determine the minimum zinc concentration solution suitable for electrowinning, with acceptable current efficiency. The electrolytic composition, Zn and H_2SO_4, were analyzed and determined, at different intervals, during the experiment. The results obtained are summarized in Table 4.12.

Table 4.12: Experimental conditions for determining the effective minimum zinc concentration in bath.

Current density	Period, hour	Efficiency %		Bath composition	
				Zn (g/L)	H_2SO_4 (g/L)
45	3	96.6	Start	120	50
45	4	93.4	End of experiment	99.2	98.4
45	4	86.3	End of experiment	69.2	140.4
45	3	53.1	End of experiment	41.2	181.6

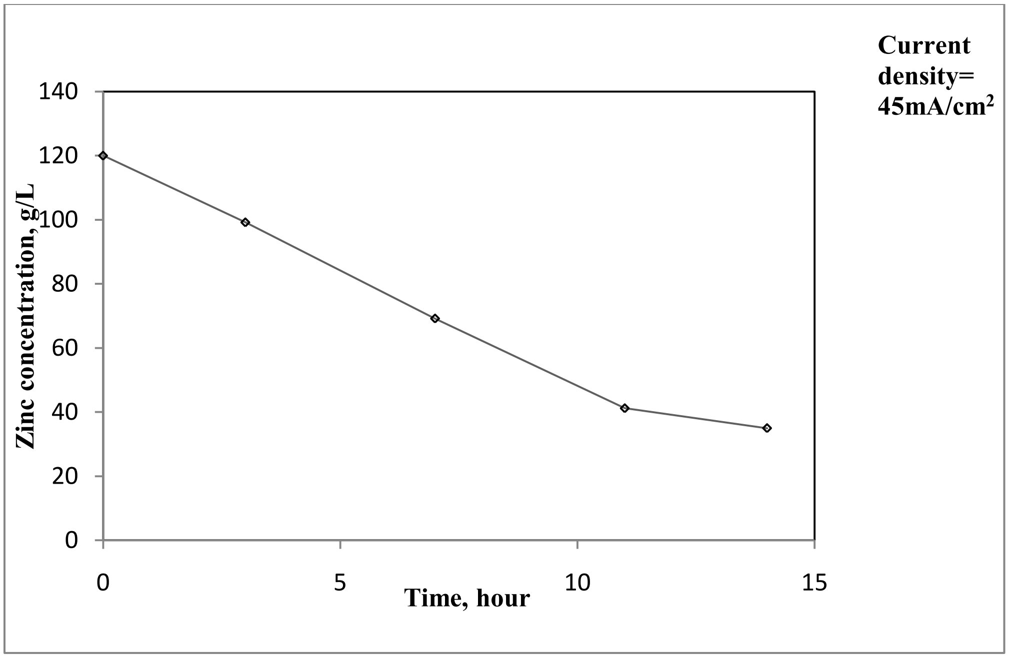


Fig. 4.17: Plot of zinc concentration vs. time.

This experiment shows that continuous removal of zinc from electrolyte, down to around 40 g/L, was achieved with current efficiency of more than 85%. Beyond this concentration a very low current efficiency was obtained. Accordingly, solutions with this range of zinc concentration (<40 g/L) should be transferred to the leaching vessel, to make use of its high acid content, for further dissolution of zinc ash.

From the results of the above table, the variation of the zinc ion concentration with time is drawn in Fig. 4.17. This figure reveals that at high concentrations the depletion rate of zinc is approximately linear and tails off as the concentration of zinc reaches 40g/L. after this, the concentration decays near exponentially.

CHAPTER 5

SUMMARY AND CONCLUSION

The extraction of zinc from discarded zinc ash through hydrometallurgical route was studied in this work.

Removal of chlorine from the zinc ash was investigated. Leaching was performed in dilute sulfuric acid solutions. Effects of the parameters like particle size of ash, concentration of leaching reagent, time of leaching and temperature of leaching were studied. The optimum conditions of leaching were established and the activation energy was determined both by the differential and the integral approaches. Conditions for satisfactory electrolysis were also determined.

The following conclusions may be derived from this investigation:

(1) Washing for 0.5 hour at 80^{o}C at liquid/solid ratio of 10:1 was adequate for satisfactory removal of chlorine.

(2) The optimum conditions for leaching were determined to be: particle size -200+270 mesh, acid concentration 3.2 M H_2SO_4, solid-liquid ratio of 1:5, duration of leaching 140 minutes and temperature 70^{o}C.

(3) Activation energy determined by differential and integral approaches was 42.89 KJ/mol (by differential approach) and 41.44 kJ/mol (by integral approach).

(4) A zinc concentration in leach liquor of 40 g/L was found to be the minimum for satisfactory electrowinning.

CHAPTER 6

RECOMMENDATION FOR FUTURE WORKS

This work emphasized on obtaining optimum process variables for leaching of zinc ash. The researchers who are interested to work on this topic may focus on the following topics.

a) Effect of stirring during leaching can be studied. This will probably ensure better extraction.
b) The activation energy can be determined including stirring in experimental set-up to observe the effect of stirring on activation energy.
c) Sulphuric acid was used for leaching in this study. Leaching with hydrochloric acid [37] or alkali can be investigated.

CHAPTER 7

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